

Organic Chemistry of Transition Metals.
I. New Reactions of Bis(arene)iron(II) Salts.
II. Synthesis and Structure of π -cyclopentadienyl- π -tetra-
phenylcyclobutadienerhodium(I).

By

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Abstract of Dissertation Presented to the
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of the Requirements for the Degree of Doctor of Philosophy

Organic Chemistry of Transition Metals.

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Major Department: Chemistry

Bis(mesitylene)iron(II) hexafluorophosphate was found to react with certain relatively weak, carbanion nucleophiles to form 1:1 adducts. Specifically, anions of the following materials were used: Hydrogen cyanide, nitromethane, nitroethane, tert-butyl acetate. Also, the anion of 2,6-di-tert-butylphenol added as though the four position were the anionic center. The adducts derived from anions of the first, second, and fourth compounds listed above were oxidized with ceric ion to give a mixture of mesitylene and a 2-substituted mesitylene. The 2-substituted mesitylenes were purified and characterized. When the adduct derived from 2,6-di-tert-butylphenoxide was so treated, no such product resulted.

When any of six nitrogen and oxygen nucleophiles were used, an adduct of the same type resulted, but it did not contain the nucleophile. Instead, it appeared to be derived from two molecules of the starting iron complex. This phenomenon was explained in terms of an initial proton abstraction step. Efforts to trap an intermediate were unsuccessful. In support of such a mechanism, however,

bis(hexamethylbenzene)iron(II) bromide was found to undergo complete proton exchange with deuterium oxide in the presence of a catalytic amount of organic base. This exchange procedure was not applicable to other methylated benzenes.

The course of the reaction of bis(mesitylene)iron(II) hexafluorophosphate with cyanide, azide, amide, or cyanate ion was found to differ markedly depending upon the presence or absence of oxygen. This phenomenon was explained in terms of a contact charge transfer complex of the organoiron cation and oxygen.

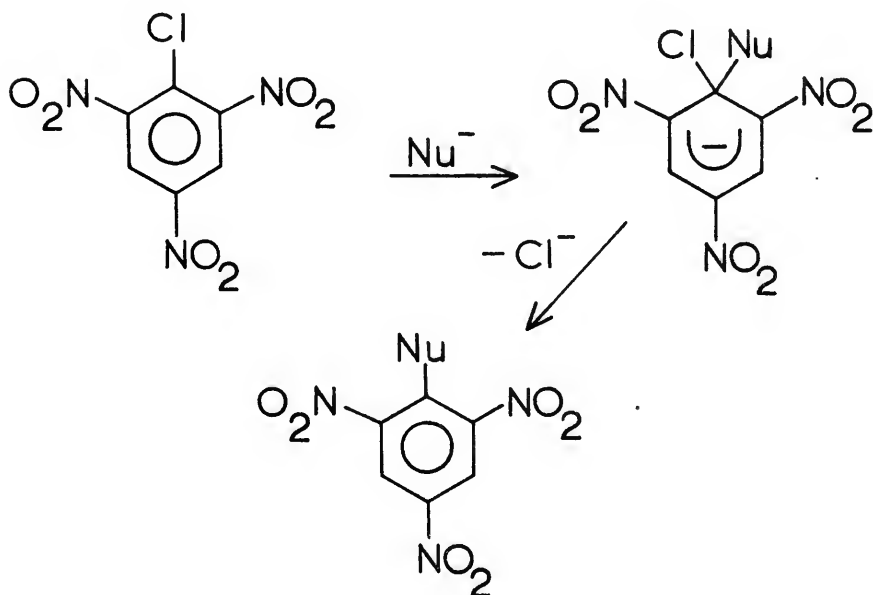
Several heteroatom nucleophiles, specifically, thiocyanate, thiophenoxide, cyanate, phenoxide, acetate, and fluoride ions, were found to cause decomposition of bis(mesitylene)iron(II) hexafluorophosphate. It is not known whether this occurs before or after addition or proton abstraction.

In the second part of the work, π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) was synthesized from π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) and diphenylacetylene. In order to rule out possible isomers, the structure was determined by X-ray diffraction methods. The crystal data were as follows: Space group: $P2_1/c$. $M = 524.26$ ($C_{33}H_{25}Rh$), $a = 13.416(3)$, $b = 19.534(6)$, $c = 13.411(2)$ Å, $\beta = 135.01(1)^\circ$, $U = 2484.6(1.1)$ Å³, $Z = 4$, $D_c = 1.411$ g/cm³, $D_m = 1.40$ g/cm³.

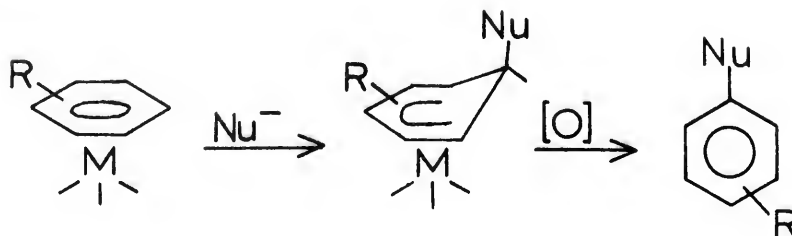
I. NEW REACTIONS OF BIS(ARENE)IRON(II) SALTS

INTRODUCTION

Nucleophilic aromatic substitution generally does not proceed readily except in the presence of electron-withdrawing substituents, e.g., nitro, nitroso, cyano, etc. Since several additional steps are required to remove these groups, nucleophilic substitution is generally not the method of choice in syntheses of arenes not containing these groups. There are, of course, exceptions. An approach which has recently found some utility in overcoming this difficulty



is the use of a pseudo-electron-withdrawing substituent which is in fact not a true substituent at all, but a transition metal ion (or atom) to which the arene has been π -complexed.¹⁻⁸



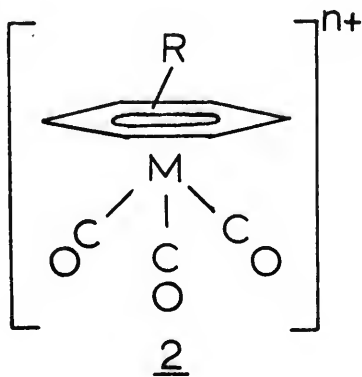
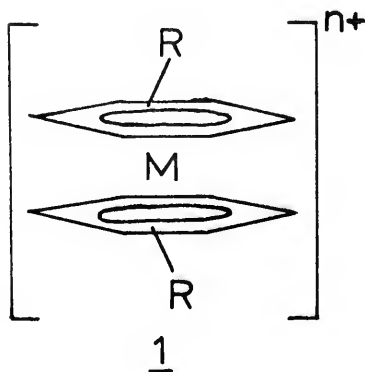
The cyclohexadienyl intermediates have often been isolated from these organometallic reactions as compounds of interest in themselves. From a purely organic synthetic standpoint, however, these intermediates could probably usually be oxidized in situ to give the substituted arene directly. In some cases this has been done.⁴⁻⁷

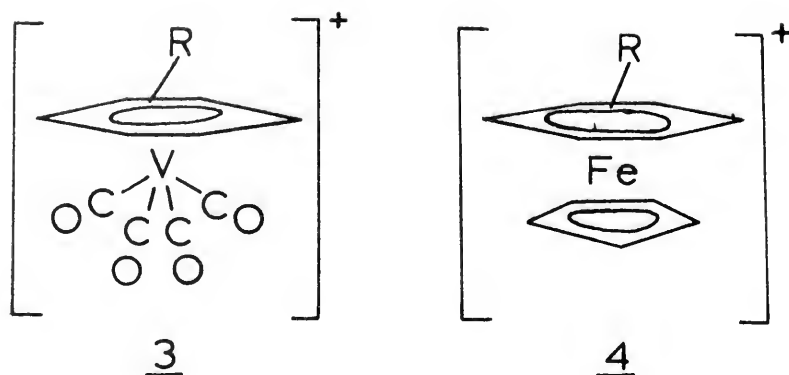
The present work was concerned with extending the scope of this method and with delineating some of its limitations. The systems studied were bis(arene)iron(II) cations in which the arenes were methylated benzenes. Some other work with these systems has appeared,^{1,2} and a portion of the present study has been published.³ Some useful extensions and clear-cut limitations of the previous work were documented, and several completely unanticipated reactions were also discovered and explored. It seems at this time that bis(arene)iron(II) salts may someday be the starting materials of choice in some organic syntheses, while for superficially similar systems the method will be inadequate. The theoretical and experimental bases for this statement follow.

CHAPTER I

BIS(ARENE)IRON(II) SALTS AS ELECTROPHILES

The synthetic potential of bis(arene)iron(II) cations (1, $M = Fe$, $n = 2$) lies in the fact that an arene which would normally exhibit nucleophilic character is altered by coordination to iron in such a way that it exhibits electrophilic character. Some synthetic work in which this alteration is utilized has already been published.¹⁻³ Similar work has also been published which utilized π -arenetricarbonylchromium(0) (2, $M = Cr$, $n = 0$)⁴⁻⁷ and π -arenetricarbonylmanganese(I) (2, $M = Mn$, $n = 1$).⁸ Although some work has appeared regarding nucleophilic addition to other arene-metal systems, viz., bis(arene)manganese(I) (1, $M = Mn$, $n = 1$),⁹ π -arenetricarbonylvandium(I) (3),¹⁰ η^5 -cyclopentadienyl- π -areneiron(II) (4),¹¹⁻¹⁵ bis(arene)rhenium(I) (1, $M = Re$, $n = 1$),¹¹ and bis(arene)ruthenium(II)

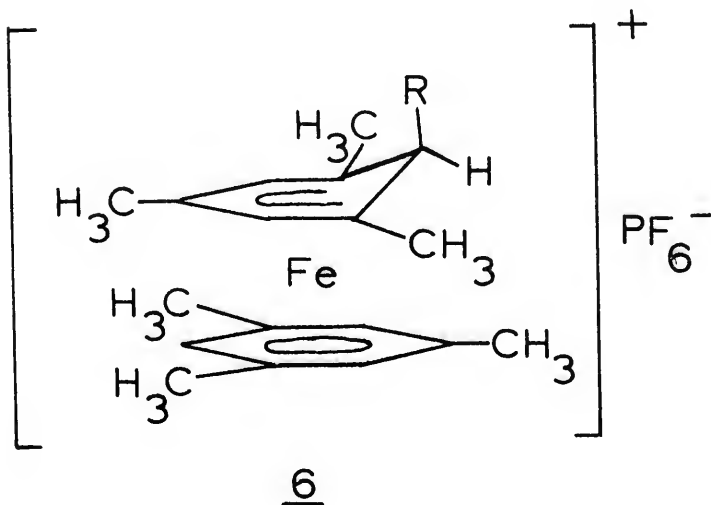
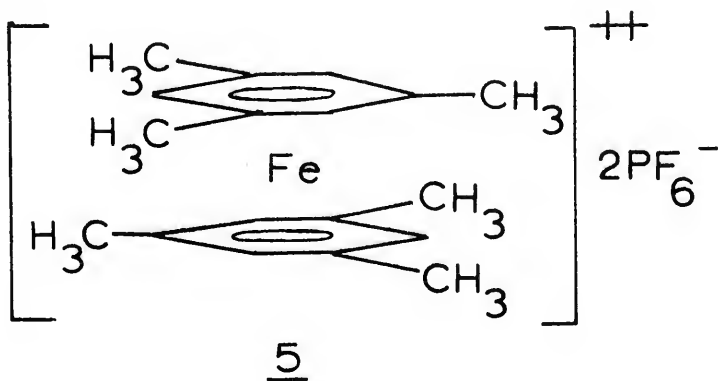




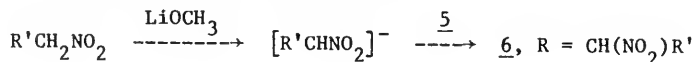
(1, $M = \text{Ru}$, $n = 2$),¹¹ potential synthetic applications were apparently largely ignored. As Semmelhack and Hall recently suggested,⁵ there may be a prejudice against the use of nucleophilic aromatic substitution as a synthetic procedure because of the difficulty associated with removal of groups (e.g., nitro) which classically rendered arenes susceptible to such substitutions.

In almost all of the previous work involving nucleophilic attack on arene-metal systems, the nucleophile was either a very reactive carbanion, i.e., an alkyl- or aryllithium, or a hydride, usually LiAlH_4 or NaBH_4 . In addition, the organolithium reagents were ones with localized anions, usually methyl or phenyl. The only reports involving partially delocalized anions are one which described the addition of the anion of diethyl malonate to π -benzenetricarbonylmanganese(I) tetrafluoroborate¹⁶ and two which dealt mostly with the interactions of various derivatives of α -lithioisobutyric acid with π -arenetricarbonylchromium(0) (2, $M = \text{Cr}$, $n = 0$).^{5,7} In the present study, several delocalized anions were

found to react with bis(mesitylene)iron(II) hexafluorophosphate (5) to give mono-adducts of the type 6. (The drawing of the rings in 5 to show staggered methyl groups is solely a matter of convenience and is not meant to imply any knowledge of the actual preferred conformation.)



Probably the most synthetically significant of these reactions were the additions of the anions of nitromethane and nitroethane. Both of these reactions were run in the nitroalkane, and the anion was generated in situ with lithium methoxide.



The yield in the nitromethyl anion addition step was unaccountably low (52%) in spite of repeated attempts. The yield in the nitroethyl anion reaction ($\underline{5} \rightarrow \underline{6}$, $\text{R} = \text{CHCH}_3\text{NO}_2$) was much higher (84%). Since bis(arene)iron(II) salts and their adducts are generally more stable in low-polarity solvents than in high-polarity ones, an improved yield might have resulted if α -lithionitromethane had been isolated and the reaction run in a different solvent. This idea was not pursued, however. π -Mesitylene- π -exo-6-nitromethyl-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate ($\underline{6}$, $\text{R} = \text{CH}_2\text{NO}_2$) was oxidized with ammonium hexanitratocerate(IV) to give a mixture of mesitylene and 2-nitromethyl-1,3,5-trimethylbenzene. The difference in volatility of these compounds was such that the mesitylene could be removed with a vacuum pump at room temperature with no loss of the nitro compound. The yield of the oxidation step was 45%; the overall yield starting from $\underline{5}$ was 23%. The only other reported route to 2-nitromethyl-1,3,5-trimethylbenzene¹⁷ used 2,4,6-trimethylphenylacetonitrile as the starting material and is, therefore, dependent upon the availability of other arylacetonitriles for extension to other compounds.

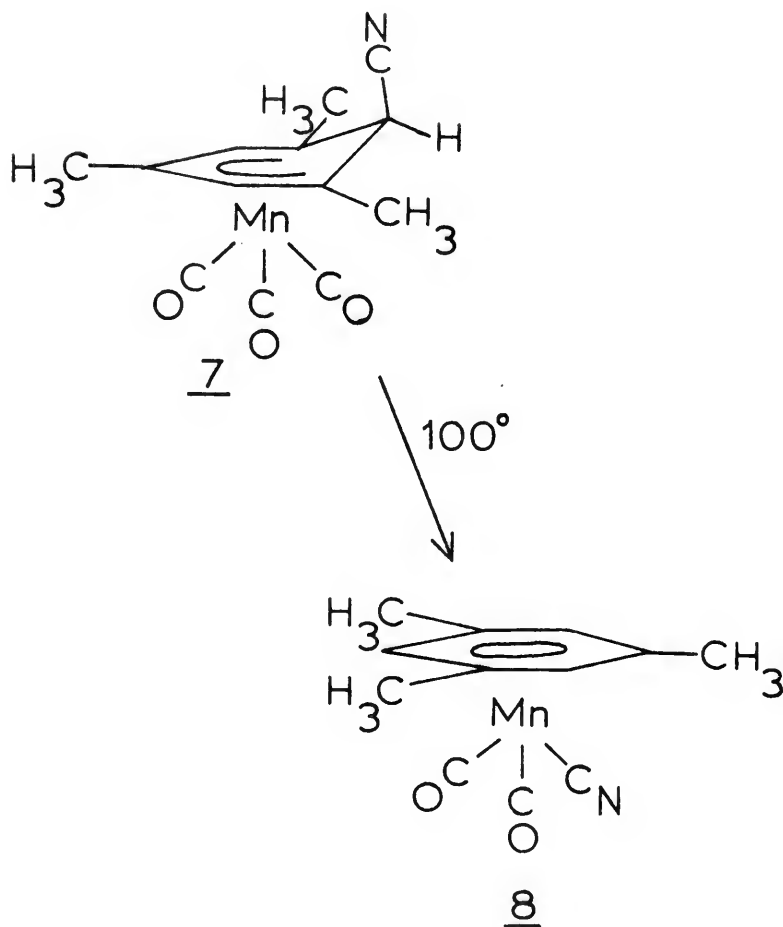
The real synthetic utility lies not in the nitro compounds themselves, but in the fact that nitro compounds can be easily con-

verted to compounds bearing other functional groups, particularly amines. Procedures have also been described for converting aliphatic nitro compounds into ketones,¹⁸ carboxylic acids,¹⁹ aldehydes,²⁰ hydroxylamines,²¹ and oximes.²² A recent review article was devoted to the use of primary nitro compounds as sources of heterocyclic systems.²³

Potassium cyanide reacted with 5 in acetone to give 6, R = CN, which was isolated and oxidized with ammonium hexanitratocerate(IV) to give a mixture of mesitylene and 2,4,6-trimethylbenzonitrile. Again, the mesitylene could simply be removed with a vacuum pump at room temperature without loss of the other compound. The addition step occurred readily and in good yield (83%). This was not surprising, since it had been reported previously that cyanide ion added to bis(hexamethylbenzene)iron(II) hexafluorophosphate to give a similar adduct.² It is also of some interest that this reaction did not occur in the absence of oxygen. Furthermore, if the adduct (6, R = CN) was evacuated overnight, it partially decomposed to a deep blue solid which was insoluble in all common solvents and was decomposed by pyridine. The infrared spectrum of this material was almost identical to that of 5, except that the former exhibited a very strong inorganic C≡N stretch at 2075 cm^{-1} . Although the blue solid could not be recrystallized, an elemental analysis of the crude material indicated that the ratio of mesitylene to cyanide was quite high, ca. three to one. No structure is obvious, and a mixture of compounds is not ruled out.

There is some precedent for rearrangement from carbon- to metal-bonded cyanide. Walker and Mawby reported that the neutral

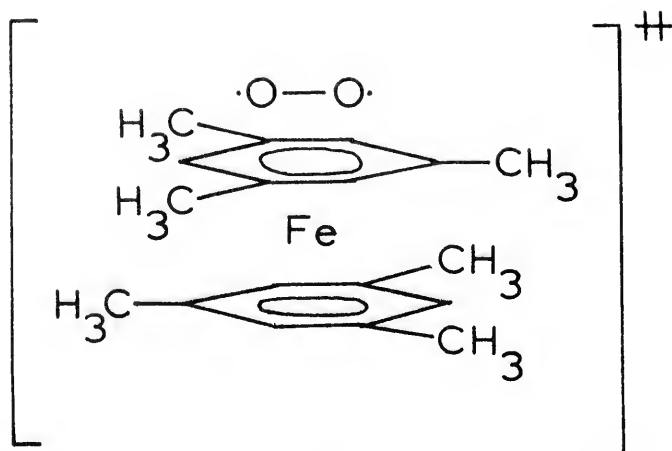
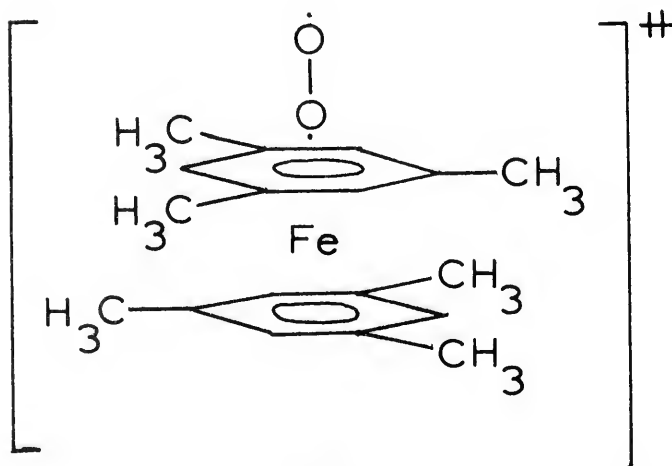
complex π -exo-6-cyano-1,3,5-trimethylcyclohexadienyltricarbonylmanganese(I) (7) rearranged on heating with evolution of carbon monoxide to give 8.²⁴



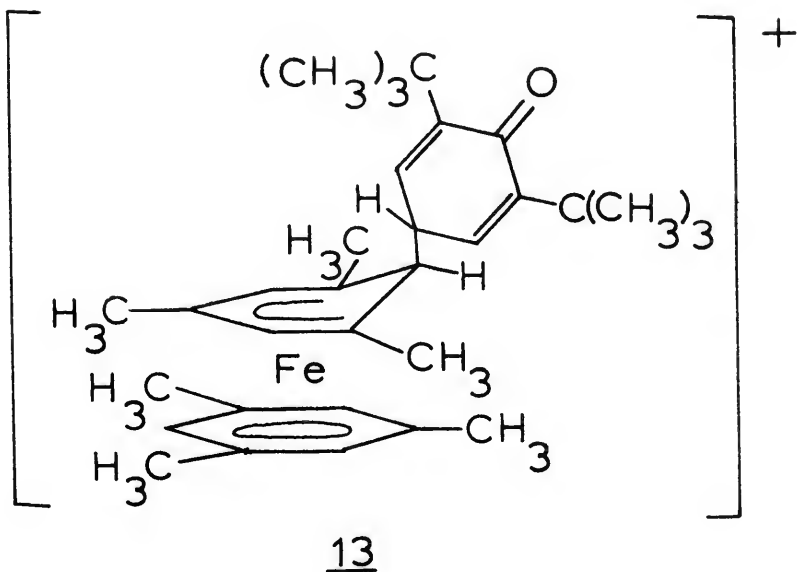
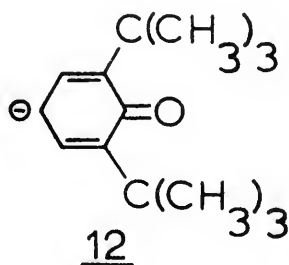
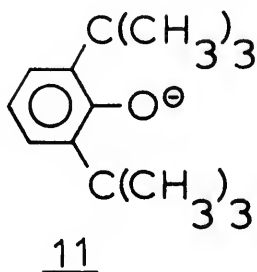
Additional evidence that there is some interaction between 5 and oxygen may be found in the fact that several other nucleophiles, namely N_3^- , NH_2^- , and NCO^- , exhibited remarkably different reactions

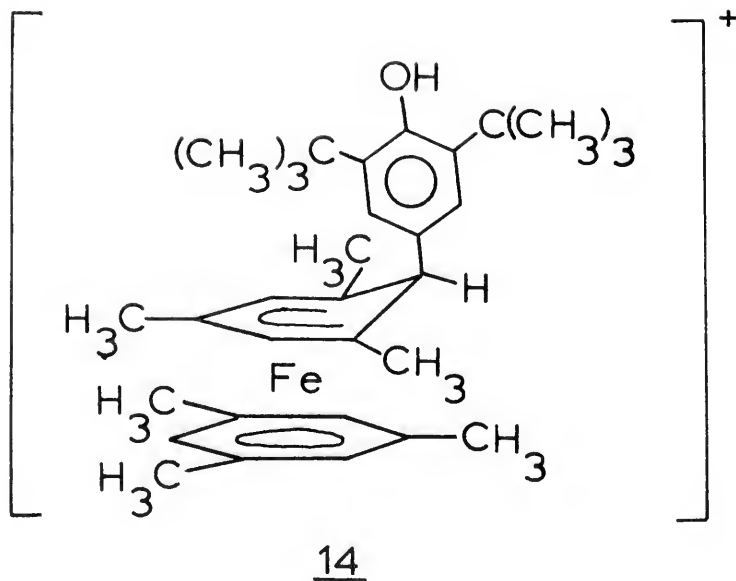
with 5 when oxygen was present than when it was absent. All of these nucleophiles (including CN^-) are sterically very small, and it seems likely that they attack the iron atom in the absence of oxygen. Since solutions of 5 in the presence and absence of oxygen exhibit no observable differences in electronic spectra, whatever interaction occurs must be quite small. Participation of nitrogen was ruled out because the reaction of 5 with lithium amide is the same under argon as under nitrogen.

What seems most likely from the available evidence is the existence in solution of "contact" charge transfer complexes²⁵⁻²⁷ of molecular oxygen and 5. Contact charge transfer complexes are charge transfer complexes which have nearly zero association energy in the ground state and are, therefore, in rapid equilibrium with their components. Molecular oxygen is known to form such complexes with a wide variety of organic electron donors such as arenes, amines, and alcohols.²⁷ These complexes were detected by their charge transfer spectra, but in some cases in which a complex was expected but not detected the charge transfer band was proposed to be totally obscured by absorption of the uncomplexed organic fragment.²⁷ Such a species could provide a suitable explanation for the present observations. Since theory requires that there be some charge transfer even in the ground state,²⁵ the charge transfer complex of 5 should be more susceptible to nucleophilic attack than is 5 alone. Also, since most of the electron density would presumably come from the arene rather than from iron, formation of a charge transfer complex should increase the probability of reaction at the arene relative to that at iron. Structures 9 and 10 depict probable orientations of the components in such a complex.

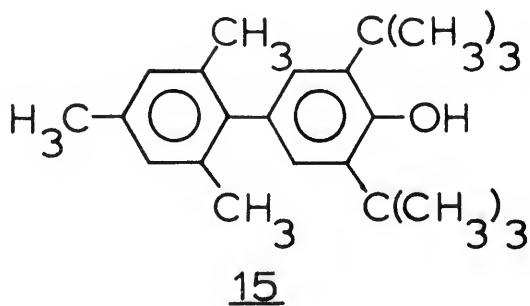
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The relatively nonnucleophilic base 2,6-di-tert-butylphenoxide (11) underwent nucleophilic addition to 5 in its resonance form 12, probably to initially form 13, which rearranged to 14 during workup.





The yield of this reaction, however, was very low (7%). Furthermore, oxidation of 14 with ceric ion gave only a very tiny amount of organic material. The expected product, 15, may have been a component of this material, but its presence was not conclusively demonstrated.



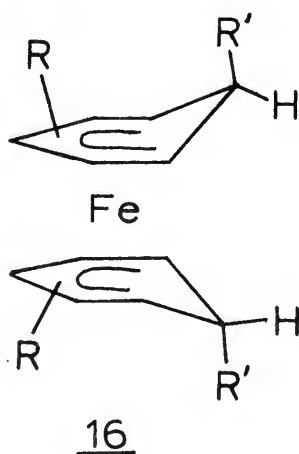
The highly substituted biphenyl 15 might have been obtained by replacing ceric ion with $(\text{CH}_3)_3\text{NO}$, an oxidizing agent which has been shown to remove iron from coordinated, easily oxidized ligands without oxidizing the ligands.^{28,29} The low yield of the addition step, however, makes this particular sequence unattractive as a synthetic procedure.

When the lithium salt of tert-butyl acetate and 5 were stirred together in dry diethyl ether, addition occurred to give 6, $\text{R} = \text{CH}_2\text{COOC}(\text{CH}_3)_3$, in 48% yield. This compound, in turn, was oxidized with ceric ion to give a 50% yield of tert-butyl 2,4,6-trimethylphenylacetate. Although this particular ester had not been reported, other esters of the same acid are available by other means.

This experiment did, however, serve to establish the reactivity of the bis(arene)iron(II) system relative to other π -arene-metal systems. Semmelhack *et al.*⁷ reported that the reaction of tert-butyl α -lithioisobutyrate and π -benzenetricarbonylchromium(0) in THF gave only a poor yield of tert-butyl α -phenylisobutyrate (ca. 10%) after oxidation of the unisolated reaction product. They were able to obtain better yields only by resorting to a different cation (potassium) or a more favorable solvent mixture (50% THF/50% HMPA). In the latter solvent system tert-butyl α -lithioisobutyrate and tert-butyl α -lithioacetate gave about the same yields of phenylated products and may, therefore, be assumed to have about the same reactivity. When these facts are all taken together, the conclusion may be drawn that bis(mesitylene)iron(II) cation is a stronger electrophile than π -benzenetricarbonylchromium(0) is.

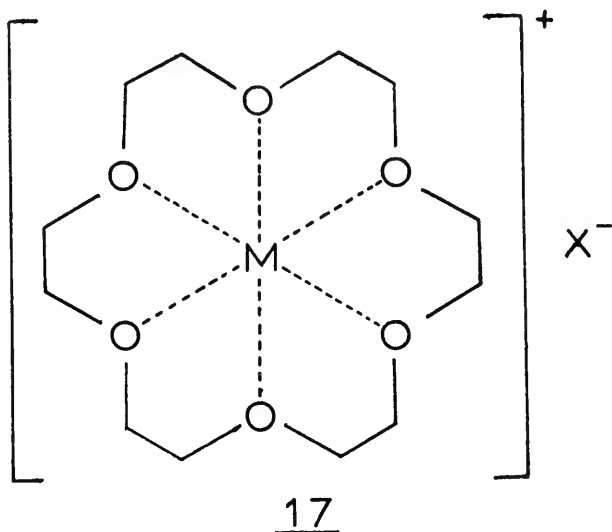
Furthermore, it should be borne in mind that bis(mesitylene)iron(II) is necessarily a weaker electrophile than bis(benzene)iron(II) is because of the electron-donating nature of the methyl groups. The electrophilicity of a system such as π -mesitylenetricarbonylchromium(0) remains to be demonstrated, although a mixture of ethylbenzene, m-ethyl-tert-butylbenzene, and p-ethyl-tert-butylbenzene (49:32:9) was obtained by addition of tert-butyllithium to π -ethylbenzene-tricarbonylchromium(0) and subsequent oxidation with ceric ion.⁴

A major problem in using the condensation of weaker nucleophiles with bis(arene)iron(II) salts as a synthetic procedure is that only mono-adducts are formed. No di-adducts such as those formed with alkyl- and aryllithium reagents (16, R' = alkyl or aryl) were observed.^{1,2} This is perhaps not surprising, since even Grignard reagents form only mono-adducts.² Surprising or not, it is very unfortunate from a synthetic standpoint because it results in effective loss of half the arene.



Several potential solutions to this problem were tried, but none was found effective. Perhaps the most obvious, i.e., simply heating the reaction mixture, was not feasible with most of the systems in the present work because bis(arene)iron(II) salts generally cannot tolerate being heated much above room temperature in solvents polar enough to dissolve them. An exception is nitroethane, a solvent of intermediate polarity, in which 6, $R = CHCH_3NO_2$, can be heated to at least 70° before beginning to decompose. However, when 5 was stirred in a solution of nitroethane and the anion thereof (generated in situ) at 60° for 45 minutes, no adducts either of the type 6 or 16 were isolated.

1,4,7,10,13,16-Heaoxacyclooctadecane, commonly known as 18-crown-6, is known to render salts such as KCN and KF soluble in organic solvents by forming a complex with the alkali metal ion (17).³⁰ It was hoped that addition of nucleophiles to 5 to

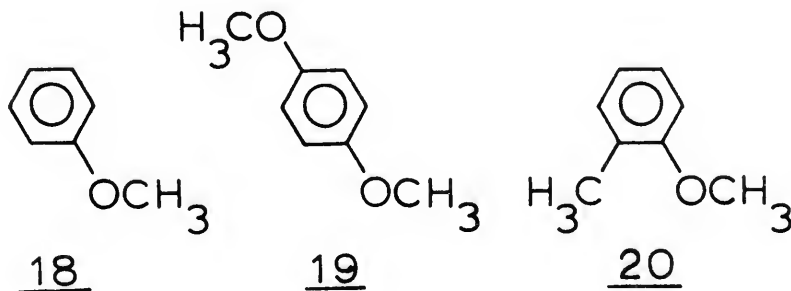


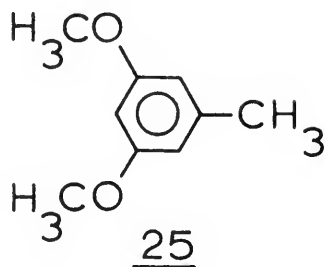
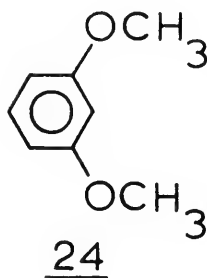
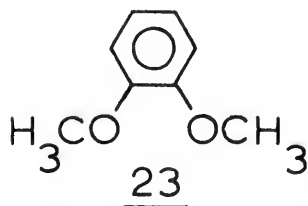
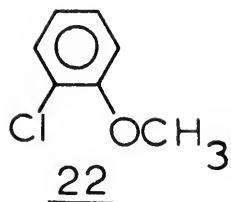
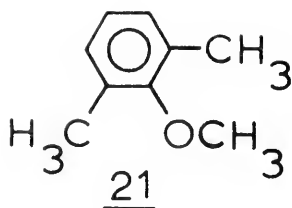
form di-adducts could be effected in refluxing benzene, in which 5 does not decompose, by using 18-crown-6 to get the nucleophile into solution. However, when 5 was refluxed overnight in benzene with either KCN or KCH_2NO_2 (generated in situ) with a catalytic amount of 18-crown-6, no di-adducts were observed. At least with KCN, the mono-adduct (6, $\text{R} = \text{CN}$) was formed, albeit in lower yield (58%) than by the more straightforward procedure (vide supra).

If the ability to form di-adducts was lost in going from stronger to weaker nucleophiles, perhaps it could be regained by increasing the strength of the electrophile. This could presumably be done by increasing the charge on the metal ion. Since bis-(arene)iron(III) species are unknown, a better choice would perhaps be bis(arene)cobalt(III) ions, which are isoelectronic with the bis(arene)iron(II) systems. Bis(arene)cobalt(III) salts were reported in a review article by Fischer and Fritz,³¹ but no experimental details were reported, and the reference was to a thesis, apparently that of one of the author's own graduate students. Several attempts to synthesize bis(mesitylene)cobalt(III) ion from mesitylene and tris(acetylacetonato)cobalt(III) in the presence of aluminum chloride failed completely. The red-brown color reported for salts of bis(mesitylene)cobalt(III) could be clearly seen in the anhydrous system, but was completely discharged when the reaction mixture was hydrolyzed. Several years after the review article in which these compounds were first reported had appeared, Fischer and another worker reported that they were unable to repeat the previous work.³² Furthermore, they were unable to synthesize by any method either the bis(arene)cobalt(III) system or the analogous bis(arene)rhodium(III)

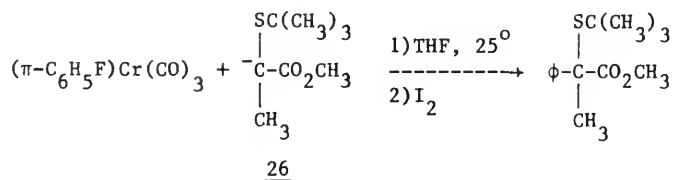
system, which should have been more stable. They therefore concluded that these systems were too labile to isolate under normal circumstances. In consideration of this report, it does not seem promising to attempt syntheses via bis(arene)cobalt(III) compounds.

At this time it is perhaps appropriate to summarize the promise of the bis(arene)iron(II) system in organic synthesis as outlined in this and other work relative to the promise of other π -arene-metal systems. A few words have already been said regarding the relative electrophilicities of bis(mesitylene)iron(II) hexafluorophosphate (5) and π -benzenetricarbonylchromium(0) (vide supra). It must be borne in mind in such a general discussion that neither the formations nor the reactions of π -arene-metal compounds are completely understood, and seemingly small changes sometimes result in dramatic differences in reaction products. A few examples will illustrate this point. Pauson et al.¹³ prepared complexes of type 4 from ferrocene and free arene when the arene was 18, 19, 20, 21, or 22, but their attempts to prepare analogous materials from 23, 24, or 25 failed.

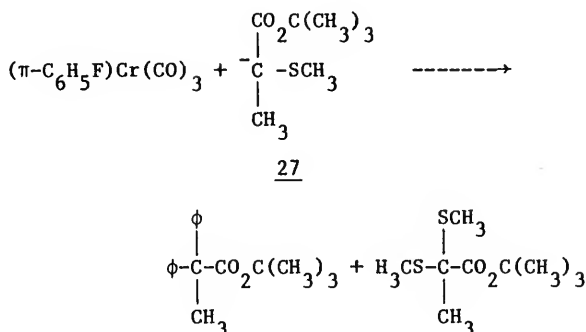




Semmelhack and Hall⁵ were able to phenylate the anion 26 by allowing it to react with π -fluorobenzenetricarbonylchromium(0) and oxidizing the intermediate.

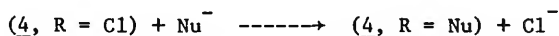


The yield was 94%. When the similar anion 27 was used under identical conditions, however, the analogous product was not obtained.



These products were isolated in approximately equal amounts. The present work with bis(arene)iron(II) ions has shown that oxygen and nitrogen nucleophiles react in an entirely different way from carbon nucleophiles. These differences will be discussed in detail in the next chapter. Remarks made by Walker and Mawby¹⁶ indicate that the π -arenetricarbonylmanganese(I) system may be similar in this regard.

Those systems for which organic synthetic reactions of the sort being discussed here have been reported are the following: π -arenetricarbonylmanganese(I), π -arenetricarbonylchromium(0), bis(arene)iron(II). Nesmeyanov *et al.*¹² also reported some addition-elimination reactions with $[(\eta^5\text{-C}_5\text{H}_5)(\pi\text{-C}_6\text{H}_5\text{Cl})\text{Fe}](\text{BF}_4)$, but did not attempt to separate the new $\text{C}_6\text{H}_5\text{X}$ ligands from the metal.



The only purely organic compound reported synthesized via the π -arenetricarbonylmanganese(I) system is 2,4,6-trimethylbenzonitrile, which was isolated in 73% yield from the oxidation of (π -exo-6-cyano-1,3,5-trimethylcyclohexadienyl)tricarbonylmanganese(I) (7) with ceric ion.⁸ This is better than the 53% yield for the same compound from 6 (vide supra), but the generality of the manganese intermediates has not been demonstrated. In summarizing the statements already made regarding the π -arenetricarbonylchromium(0) system, let it suffice to say that that system is a less active electrophile than the bis(arene)iron(II) system and that the work done to date with the two systems has been largely nonoverlapping. The former system has been used mostly for "phenylation" of nucleophiles,⁵⁻⁷ while the latter has been used mostly for "mesitylation" or "pentamethylphenylation."¹⁻³

CHAPTER II

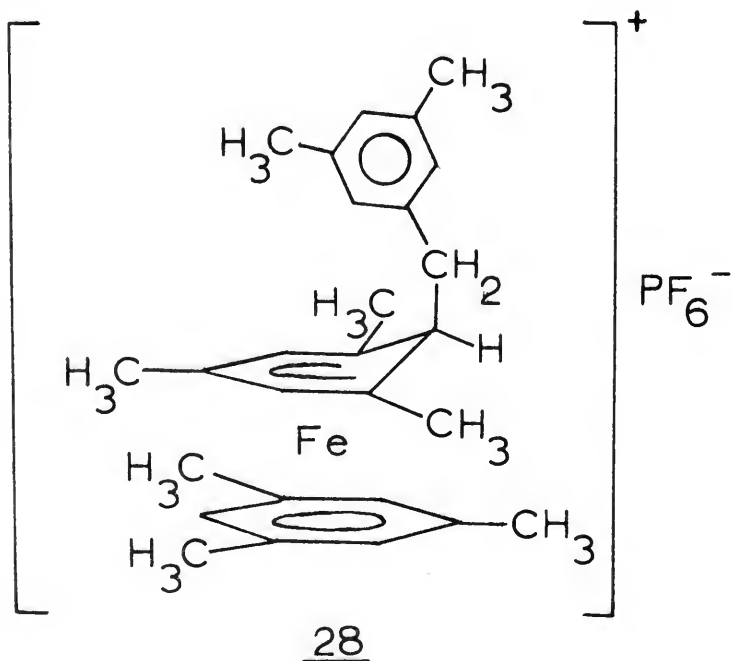
BIS(ARENE)IRON(II) SALTS AS ACIDS

In the preceding chapter was discussed one consequence of the electron-withdrawing effect of an iron(II) cation coordinated to a normally electron-rich arene, i.e., the arene is rendered susceptible to nucleophilic attack. In the present chapter a second consequence will be discussed. This consequence is that the alpha hydrogens of the coordinated arene are rendered more acidic. Thus, just as p-nitroaniline is a weaker base than aniline (and, therefore, forms a stronger conjugate acid), so bis(mesitylene)iron(II) cation is expected to be a stronger acid than mesitylene.

Only a very limited amount of work regarding the acidity of arene-transition metal complexes has been published. Part of the present work has appeared elsewhere,³ and some work with complexes of the type 4 has also been done.³³ The present interest in the acidity of bis(arene)iron(II) salts came about as the result of attempts to add oxygen and nitrogen nucleophiles to 5. When 5 was allowed to react with N_3^- , NH_2^- , $\text{N}(\text{CH}_3)_2^-$, $\text{N}[\text{Si}(\text{CH}_3)_3]_2^-$, OCH_3^- , or $\text{OC}(\text{CH}_3)_3^-$ (in various solvents, depending on the nucleophile), products were isolated which appeared to be of the type 6, but which always differed in some way from the expected product. An elemental analysis of the product isolated from the "addition" of azide ion, for example, revealed a complete absence of nitrogen. An NMR spectrum

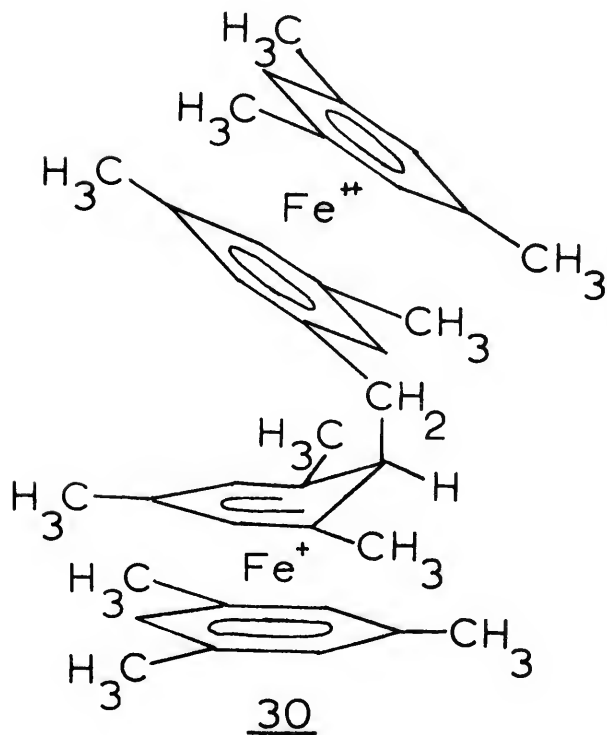
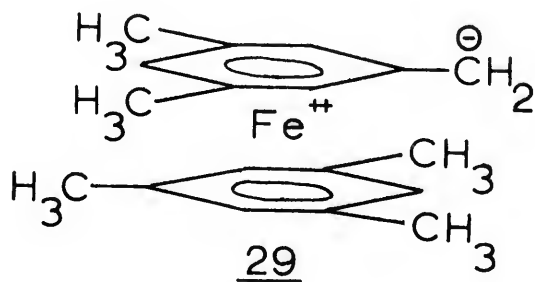
of the product from the tert-butoxide reaction displayed the group of methyl resonances typical of 6, but conspicuously lacked a tert-butyl resonance. After many unproductive thoughts and experiments, a comparison of NMR spectra revealed the reason for the anomalies. Each of the six nucleophiles listed above gave the same product, which thus necessarily did not contain the nucleophilic "addend."

The rather complex but unvarying NMR spectrum, the mass spectral peak at m/e 238, and the elemental analysis, which showed an unusually high carbon and hydrogen content for a compound of the type 6, led to the assignment of 28 as the structure for this product.



This material is envisioned to arise from an initial proton abstraction by the nucleophile from 5 to form 29 followed by attack of 29 on a

second cation 5 to form 30. Finally, one iron atom is cleaved from 30, perhaps by atmospheric oxygen (vide infra), to give 28.



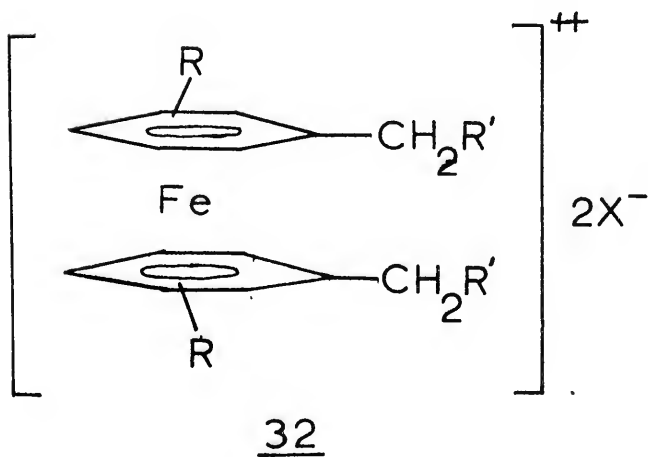
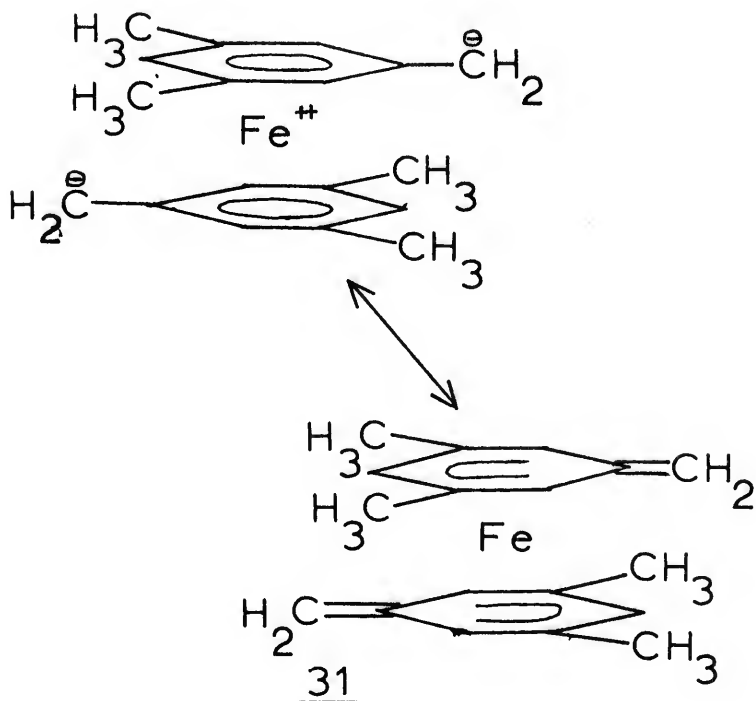
Most of these reactions were run in inert solvents such as benzene, THF, or diethyl ether, under nitrogen. Under these conditions the solvent took on a very deep red color almost as soon as the reactants were stirred together. The color was not transient, but persisted until air was admitted, at which time the color left the solution and a precipitate formed. As mentioned in the preceding chapter, N_3^- and NH_2^- required the continuous presence of oxygen for the formation of any identifiable organoiron product. In these reactions the color typical of the oxygen-free systems was not observed.

A structure for the colored material which enters benzene or diethyl ether is not entirely certain. A simple, twice-deprotonated derivative of 5, such as 31, is the obvious choice, but some experimental considerations argue against it.

If a solution of 31 were allowed to react with an electrophile such as CH_3I , Br_2 , ICl , CH_3COCl , etc., simple displacement of halide should result, and the product should be a bis(arene)iron(II) halide (32). A large number of such experiments were carried out, most of them utilizing bis(hexamethylbenzene)iron(II) bromide as the starting material instead of 5, and in no case was a product identifiable as the expected bis(arene)iron(II) halide isolated.

No reaction occurred with methyl iodide. Bromine gave a material with the wrong solubility properties; the mass spectrum of this material showed a mixture of hexamethylbenzene and brominated hexamethylbenzenes containing up to five bromine atoms. Iodine monochloride gave a tiny amount of product, the mass spectrum of which showed a great deal of hexamethylbenzene but no pentamethylbenzyl iodide. Acetyl chloride gave a small amount of product

which exhibited no obvious carbonyl stretch in the IR and no peak attributable to pentamethylphenylacetone in the mass spectrum.



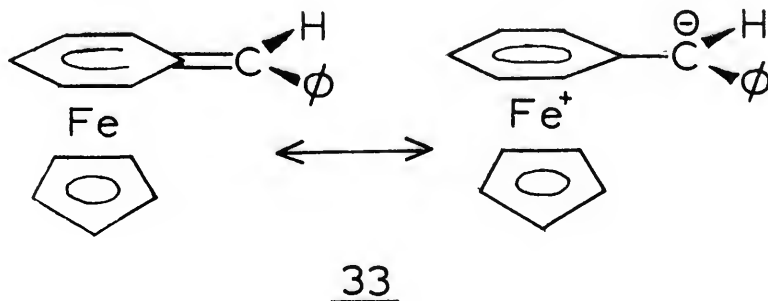
Attempted reaction with Simmons-Smith reagent to give the spiro ligands failed also. Furthermore, reaction with D_2O acidified with HCl did not lead to deuterium incorporation sufficient to be detected by mass spectrometry.

Attempts at direct isolation of species such as 31 also failed to elucidate the structure. When column chromatography through alumina or silica gel under nitrogen was attempted, only decomposition resulted. No organoiron compounds could be eluted. When bis(hexamethylbenzene)iron(II) bromide and $NaN[Si(CH_3)_3]_2$ were ground together in the solid state, a reaction was indicated by darkening of the iron complex, but only hexamethylbenzene could be sublimed from the mixture. In the only experiment in which material was apparently isolated, the intermediate was generated in ether, filtered in a dry box, and evaporated to dryness with a vacuum pump. The resulting solid dissolved in benzene- d_6 to give a colored solution, presumably of hexamethylbenzene and the hexamethylbenzene analog of 31. An NMR spectrum, however, gave no compelling evidence for such a formulation (see Experimental).

None of these results suggests the existence of a species such as 31. It is particularly difficult to interpret the result of the D_2O/HCl experiment in terms of an intermediate such as 31. It seems reasonable to assume that a relatively uncomplicated chemical entity such as 31 should exhibit relatively uncomplicated chemistry. Experimentally this has not been found to be the case.

On the other hand, there is no other structure which readily suggests itself. Solubility in nonpolar solvents precludes salts from consideration. Helling and Hendrickson³³ have presented evidence

for the existence of 33, formed by deprotonation of η^5 -cyclopentadienyl- π -diphenylmethaneiron(II) cation. Many examples have already been cited, however, both from the present work and from the literature, of the pitfalls of placing too much faith in extrapolations in arene-transition metal chemistry. In summary, it seems reasonable to say only that, while the best available explanation for the formation of 28 invokes the intermediacy of 31, 31 is only implicated and not supported by hard evidence.

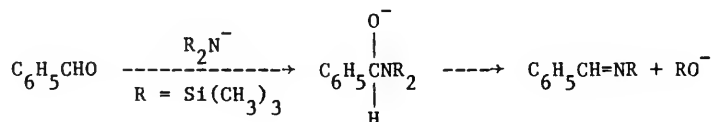


One attempt to trap 31 led to the discovery of a quite unexpected reaction. It was hoped that, if 31 were generated in the presence of a large excess of benzaldehyde, workup would yield a condensate. The base used in this reaction was $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$. No product identifiable as the desired condensate was isolated, but the most abundant product was identified as benzyl benzoate. When the reaction was repeated using mesitylene, expected to be too weakly acidic to react with the amide, in place of the iron complex, the yield of benzyl benzoate was 375% based upon the amide.

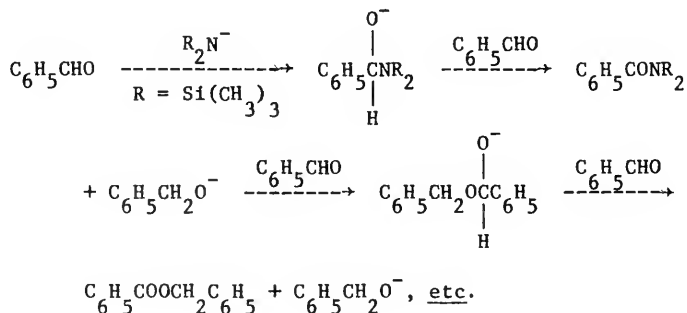
When Krüger et al.³⁴ treated benzaldehyde with a stoichiometric

amount of $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$, they isolated a 61% yield of the imine $\text{C}_6\text{H}_5\text{CH}=\text{NSi}(\text{CH}_3)_3$. They did not report whether benzyl benzoate was isolated. These workers also reported that the anion of trimethylsilanol is generated in this reaction.

If one assumes that addition to form the tetrahedral intermediate is fast and elimination of $(\text{CH}_3)_3\text{SiO}^-$ is slow, the difference between the two cases becomes obvious. In the stoichiometric reaction there is no excess aldehyde to accept a hydride ion in Cannizzaro fashion, and elimination eventually occurs.



When an excess of aldehyde is present, however, hydride transfer occurs.



The disproportionation of benzaldehyde to benzyl benzoate, catalyzed by the anion of benzyl alcohol, has been shown to proceed with 90-93% conversion to ester.³⁵ This reaction, called the Tishchenko reaction, is also catalyzed by aluminum trialkoxides.^{36,37} In view of the excellent yield obtainable by other means, it is doubtful whether

the present reaction is at this time likely to be of great synthetic value.

Another reaction which arose from the present study, however, does represent a significant improvement over published methods. This is the deuteration of hexamethylbenzene in the form of bis(hexamethylbenzene)iron(II) bromide with D_2O in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane. Exchange of all 36 protons per cation was 75% complete after 90 minutes at room temperature and 94% complete after 24 hours based upon NMR and mass spectral measurements. Previous methods for deuterating hexamethylbenzene involved the use of either KND_2 and liquid ND_3 ³⁸ or CF_3COOD at 70° .³⁹ Both of these systems are costly and difficult to work with compared to D_2O . In a control experiment, mass spectral analysis showed no detectable proton exchange of uncoordinated hexamethylbenzene with 5% D_2O in DMF containing the same catalyst after 20 hours at room temperature. Unfortunately, this procedure does not appear to be applicable to other methylated benzenes, i.e., pentamethylbenzene, durene, or mesitylene, since the corresponding iron salts decompose rapidly in aqueous base.

Several nucleophiles which might have been expected to elicit acidic behavior from bis(mesitylene)iron(II) cation instead caused only decomposition. These were thiocyanate, thiophenoxide, cyanate, phenoxide, acetate, and fluoride.

CHAPTER III

EXPERIMENTAL

Melting points were taken in evacuated, sealed capillary tubes on a Thomas-Hoover Melting Point Apparatus; these are uncorrected. All solvents referred to as dry were distilled from calcium hydride immediately prior to use with the exception of methanol, which was distilled from a solution of sodium methoxide in methanol. All reagents were commercially available reagent grade materials unless otherwise described.

Elemental analyses were performed by PCR, Incorporated, Gainesville, Florida, or by Atlantic Microlab, Incorporated, Atlanta, Georgia.

NMR spectra were recorded on a Varian A60-A 60 MHz spectrometer using internal tetramethylsilane as a standard. The following abbreviations are used in describing the spectra: s for singlet, d for doublet, t for triplet, q for quartet, m for multiplet.

Infrared spectra were recorded on either a Beckman IR-10 or a Perkin-Elmer 337 spectrophotometer.

Ultraviolet-visible spectra were recorded on a Cary 15 instrument.

Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6E single-focussing mass spectrometer at 70 ev.

π -Mesitylene- π -(exo-6-cyano-1,3,5-trimethylcyclohexadienyl)iron(II)
Hexafluorophosphate

Bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) and KCN (0.13 g, 2.0 mmol) were stirred together in 50 ml of acetone. No precautions were taken to exclude air. As the reaction progressed, the crystals of KCN turned black and the solution darkened. After 30 minutes most of the solid had disappeared. At this time the acetone was evaporated of a rotary evaporator. The residue was taken up in a minimum amount of CH_2Cl_2 , filtered, and treated with several volumes of diethyl ether. The resulting orange precipitate was collected on a filter and dried under vacuum for one hour. The yield was 390 mg (83%).

^1H NMR spectrum (τ , acetone- d_6): 4.01(s,3), 5.27(s,2), 6.09(s,1), 7.19(s,3), 7.50(s,9), 8.25(s,6). IR (KBr pellet): 2990(w), 2930(w), 2240(w, alkyl C \equiv N stretch), 1537(m), 1452(m), 1387(m), 1308(m), 1040(m), 1009(m), 962(w), 919(m), 850(s), 838(vs), 740(w), 640(w), 556(s), 490(m), 400(m) cm^{-1} .

π -Mesitylene- π -(exo-6-nitromethyl-1,3,5-trimethylcyclohexadienyl)-
iron(II) Hexafluorophosphate

Lithium methoxide (76 mg, 2.0 mmol) was dissolved in 20 ml of dry methanol. Thirty milliliters of nitromethane were then added. This solution was added dropwise to a stirred solution of bis-(mesitylene)iron(II) hexafluorophosphate (293 mg, 0.5 mmol) in 50 ml of nitromethane. During the addition the solution became noticeably darker, then somewhat lighter again. Immediately following the addition, which took 20 minutes, the entire solution was poured into 600 ml of technical grade diethyl ether and filtered to give a pale yellow solution and an orange solid. The solid was extracted

with CH_2Cl_2 and filtered to give a red-orange solution and a small amount of a tan solid. Partial evaporation of the CH_2Cl_2 and addition of ca. three volumes of diethyl ether precipitated the product (130 mg, 52%), an orange solid.

^1H NMR spectrum (τ , acetone- d_6): 4.11(s,3), 5.50(s,2), 6.39(m,3), 7.28(s,3), 7.50(s,9), 8.27(s,6). IR (KBr pellet): 3050(w), 3030(w), 2980(w), 2945(w), 2905(w), 1553(s), 1437(m, broad), 1372(s), 1199(m), 1032(s), 925(w), 871(m), 830(vs), 550(s), 500(w), 484(w), 469(w), 396(m) cm^{-1} .

π -Mesitylene- π -[exo-6-(1-nitroethyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate

A solution of lithium methoxide (152 mg, 4.0 mmol) in a mixture of 30 ml of dry methanol and 30 ml of nitroethane was added over a period of 30 seconds to a stirred solution of bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) in 100 ml of nitroethane. During the addition the solution turned dark red and a white solid precipitated. The reaction mixture was treated with 1500 ml of technical grade diethyl ether and filtered. The resulting solid was extracted with CH_2Cl_2 to give a red solution. Addition of several volumes of diethyl ether to this solution caused precipitation of the product, an orange solid, which was collected by filtration and dried under vacuum. The yield was 0.44 g (84%).

^1H NMR spectrum (τ , acetone- d_6): 4.14(s,3), 5.50(s,2), 6.23(d of q,1), 6.59(d,1), 7.31(s,3), 7.59(s,9), 8.26(s,6), 8.95(d,3). IR (KBr pellet): 3100(w), 3060(w), 2995(w), 2950(w), 1535(s), 1453(m), 1386(m), 1360(w), 1310(w), 1037(m), 870(m), 830(vs), 551(s), 512(w), 498(w), 475(w), 444(w), 415(w), 396(w) cm^{-1} .

π -Mesitylene- π -[exo-6-(3,5-dimethylbenzyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate

A. Benzene (40 ml) was distilled from CaH_2 into a flask containing 0.61 g (3.3 mmol) of $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$.⁴⁰ A magnetic stirring bar and 0.98 g (1.65 mmol) of bis(mesitylene)iron(II) hexafluorophosphate were added under nitrogen. The benzene took on a deep red color almost immediately. The mixture was stirred for 75 minutes and then evaporated to a gummy brown solid on a rotary evaporator. This solid was stirred with 40 ml of chloroform and filtered to give a red solution. Partial evaporation of this solution and addition of ca. 100 ml of diethyl ether gave the orange product, which was isolated in a yield of 36% (164 mg).

^1H NMR spectrum (τ , acetone- d_6): 3.23 (broad s, 1), 3.53 (broad s, 2), 4.33 (s, 3), 5.80 (s, 2), 7.03 (poorly resolved t, $J = 6$ Hz, 1), 7.43 (s, 3), 7.60 (s, 9), 7.82 (s, 6), 8.22 (d, $J = 6$ Hz, 2), 8.48 (s, 6). IR (KBr pellet): 3100(w), 3060(w), 2970(w), 2910(w), 1603(w, broad), 1533(w), 1453(m), 1385(m), 1307(w), 1141(w), 1035(m), 835(vs), 553(s), 493(w), 465(w), 396(w, broad) cm^{-1} .

B. Bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) and lithium amide (115 mg, 5.0 mmol) were stirred together for 48 hours in 50 ml of refluxing, dry THF in a round-bottom flask fitted with a condenser and a drying tube. The THF was evaporated, and the residue was worked up in the manner described in Procedure A. This reaction yielded 30 mg of product (11%). Identification was made by NMR.

C. Bis(mesitylene)iron(II) hexafluorophosphate (3.52 g, 6.0 mmol) was transferred under nitrogen into a round-bottom flask containing a large molar excess of $\text{LiN}(\text{CH}_3)_2$ and 100 ml of dry benzene. The

reactants were stirred together for one hour, after which time the benzene was evaporated to give a brown, gummy residue. This residue was extracted with chloroform and filtered. After the red CHCl_3 solution had been evaporated to dryness, the residue was dissolved in a 1:5 mixture of acetone and CH_2Cl_2 and chromatographed through 13 cm of silica gel. The resulting red solution was partially evaporated and treated with several volumes of diethyl ether to give the orange solid product in 34% yield (570 mg). Identification was made by NMR.

D. To a stirred solution of 0.59 g (1.0 mmol) of bis(mesitylene)-iron(II) hexafluorophosphate in 50 ml of acetone was added 0.13 g (2.0 mmol) of NaN_3 . The solution began to darken within one minute. After 15 minutes the acetone was removed with a rotary evaporator, and the residue was stirred with CH_2Cl_2 . Filtration of the resulting mixture gave a yellow-orange solution and a reddish-brown solid. The solution was evaporated to a volume of a few milliliters and treated with 50 ml of diethyl ether. An orange precipitate was separated by filtration, washed with ether, and dried under vacuum. The product (30 mg, 11%) had an NMR spectrum identical to that of the product obtained in Procedure A.

E. Fifty milliliters of THF were distilled from CaH_2 into a 100-ml round-bottom flask containing a magnetic stirring bar. Bis-mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) was added, a drying tube was fitted onto the flask, and the mixture was stirred until a slurry formed. The drying tube was removed long enough to permit the introduction of solid potassium tert-butoxide (0.17 g, 1.5 mmol) and then replaced. After 20 hours of stirring, the mixture

was evaporated on a rotary evaporator to dryness, extracted with CH_2Cl_2 , and filtered. The resulting red solution was reduced somewhat in volume and treated with several volumes of diethyl ether to precipitate the product. Filtration and vacuum drying gave a yield of 280 mg (19%). The product was identified by NMR.

F. Bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) was added a little at a time to a stirred solution of lithium methoxide (76 mg, 2.0 mmol) in 60 ml of dry methanol. As the reaction progressed, the solution became very dark red. After five minutes the reaction mixture was filtered. The red solution which resulted was evaporated until a solid began to form and then cooled in an ice-acetone bath for three hours. The solid was collected by filtration, washed with ether, and recrystallized to yield 60 mg of product (20%). Identification was made by NMR.

π -Mesitylene- π -[exo-6-(4-hydroxy-2,6-di-tert-butylphenyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate

Bis(mesitylene)iron(II) hexafluorophosphate (2.05 g, 3.5 mmol) was added to a stirred solution of potassium 2,6-di-tert-butylphenoxide (0.93 g, 3.8 mmol) in 100 ml of dry THF under nitrogen. After 45 minutes of stirring, the THF was removed with a rotary evaporator. The residue was extracted with CH_2Cl_2 and filtered to give a red-orange solution and a tan solid. The solution was partially evaporated and treated with several volumes of diethyl ether to precipitate the orange product. This precipitate was collected and dried under vacuum to yield 153 mg (6.8%).

^1H NMR spectrum (τ , acetone- d_6): 3.52(s,2), 4.14(s,3), 5.53(s,2), 6.18(s,1), 7.29(s,3), 7.50(s,10), 8.36(s,6), 8.69(s,18). IR (KBr

pellet): 3610(s, OH stretch), 2960(s), 2910(m), 2880(m), 1620(w, broad), 1535(m), 1432(s), 1385(s), 1309(m), 1235(m), 1208(m), 1188(w), 1160(m), 1121(m), 1035(s), 903(m), 830(vs), 771(w), 741(w), 566(s), 498(w), 479(m), 439(m), 400(m) cm^{-1} .

π -Mesitylene- π -[exo-6-(tert-butoxycarbonylmethyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate

Bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) was added to a stirred suspension of α -lithio-tert-butyl acetate (0.22 g, 1.8 mmol) in 50 ml of dry diethyl ether under nitrogen.⁴¹ After one hour of stirring, the reaction mixture had turned dark. It was filtered to give a light yellow solution and an orange solid. The solid was washed through the filter with CH_2Cl_2 to give a red-orange solution and some insoluble orange material. The CH_2Cl_2 solution was treated with several volumes of diethyl ether, and the orange product precipitated. This product was collected and dried under vacuum to yield 269 mg (48%).

^1H NMR spectrum (τ , acetone- d_6): 4.20(s,3), 5.65(s,2), 6.96(t,1), 7.26(s,3), 7.54(s,9), 8.33(s,6), 8.63(d,2), 8.67(s,9). IR (KBr pellet): 2970(m), 2920(w), 1728(s, alkyl ester C=O stretch), 1534(m), 1445(m, broad), 1408(w), 1391(m), 1381(m), 1369(m), 1360(m), 1305(m), 1250(m), 1161(s), 1039(m), 876(m), 832(vs), 654(w), 556(s), 473(m), 405(m) cm^{-1} .

Oxidation of π -Mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) Hexafluorophosphate

Solutions of π -mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate (370 mg, 0.8 mmol) in 50 ml of CH_2Cl_2 and ammonium hexanitratocerate(IV) (2.74 g, 5.0 mmol) in 50 ml of water were shaken together for 20 minutes in a separatory funnel. During this time the organic phase changed from medium

orange to nearly colorless. The organic layer was removed, and the aqueous layer was washed with 25 ml of CH_2Cl_2 . The combined CH_2Cl_2 layers were dried over MgSO_4 , filtered, and evaporated to give a colorless oil and a small amount of orange solid, presumably unreacted starting material. The oil was taken up in pentane and filtered to eliminate the orange solid. The pentane was evaporated to give a mixture of colorless oil and white crystals. An NMR spectrum of this mixture in CCl_4 showed that if mesitylene and 2,4,6-trimethylbenzonitrile were assumed to be the only hydrogen-containing species present, the proportions were 82% 2,4,6-trimethylbenzonitrile and only 28% mesitylene. Presumably some of the more volatile mesitylene was lost in removal of the solvents. Evacuation to 0.05 torr at room temperature for 45 minutes left only white crystals (61.4 mg, 53%), identified as 2,4,6-trimethylbenzonitrile by NMR (τ values in CCl_4 : 3.14(s,2), 7.55(s,6), 7.70(s,3)), IR (KBr pellet: $\text{C}\equiv\text{N}$ stretch at 2190 cm^{-1}), and melting point ($49-51^\circ$, lit.⁴² $50-2^\circ$).

Oxidation of π -Mesitylene- π -exo-6-nitromethyl-1,3,5-trimethylcyclohexadienyliron(II) Hexafluorophosphate

π -Mesitylene- π -exo-6-nitromethyl-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate (275 mg, 0.55 mmol) was dissolved in a mixture of 20 ml of CH_2Cl_2 and 10 ml of acetone. This solution was shaken in a separatory funnel with a solution of ammonium hexanitratocerate(IV) (1.65 g, 3.0 mmol) in 15 ml of water. The organic phase lost its color, but contained a white suspension. The organic layer was separated, and the suspension was dissolved by adding 20 ml of acetone. The resulting solution was dried over MgSO_4 , filtered, and evaporated to a colorless oil. The NMR spectrum of this oil in

CCl_4 suggested that it was composed of 79% 2-nitromethyl-1,3,5-trimethylbenzene and 21% mesitylene. Again, some mesitylene was presumed to have been lost during solvent removal. Evacuation to 0.05 torr at room temperature for two hours left white crystals (44.5 mg, 45%) of 2-nitromethyl-1,3,5-trimethylbenzene (m.p. $67-90^\circ$, lit.¹⁷ $70-1^\circ$).

^1H NMR spectrum (τ , acetone- d_6): 3.13(s,2), 4.52(s,2), 7.63(s,6), 7.71(s,3). IR (KBr pellet): 3010(w), 2975(w), 2955(w), 2915(w), 2060(w), 1613(s), 1583(m), 1550(vs, alkyl NO_2), 1485(w), 1454(s), 1422(m), 1365(s, alkyl NO_2), 1314(m), 1295(m), 1252(w), 1215(m), 1207(w), 1147(w), 1035(m), 1020(w), 887(m), 866(s), 832(s), 741(s), 692(s), 590(m) cm^{-1} .

Oxidation of π -Mesitylene- π -[exo-6-(tert-butoxycarbonylmethyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate

Solutions of π -mesitylene- π -[exo-6-(tert-butoxycarbonylmethyl)-1,3,5-trimethylcyclohexadienyl]iron(II) hexafluorophosphate (556 mg, 1.0 mmol) in 25 ml of CH_2Cl_2 and ammonium hexanitratocerate(IV) (3.29 g, 6.0 mmol) in 50 ml of water were shaken together for 20 minutes in a separatory funnel, during which time the organic layer lost its color. The resulting mixture was filtered to help disperse the emulsion which had formed. The layers were separated, and the aqueous layer was washed with 25 ml of CH_2Cl_2 . The combined CH_2Cl_2 layers were dried over MgSO_4 , filtered, and evaporated to give an orange oil. Addition of 20 ml of pentane caused a small amount of orange solid to precipitate. This solid was removed by filtration, and the pentane was evaporated. The resulting straw-colored oil was identified by NMR as a mixture of mesitylene and tert-butyl (2,4,6-trimethylphenyl)acetate. Evacuation to 0.05 torr for several hours

at room temperature removed the mesitylene, leaving the yellow liquid ester (117 mg, 50%).

^1H NMR spectrum (τ , CCl_4): 3.31(s,2), 6.58(s,2), 7.75 and 7.80 (two overlapping s, larger one downfield, combined area 9), 8.62(s,9). IR (neat liquid): 3000(m), 2970(s), 2920(s), 2865(m), 2730(w), 1765(m), 1725(vs), 1612(m), 1580(w), 1482(m), 1445(s), 1415(w), 1391(m), 1366(s), 1330(s), 1299(w), 1245(s), 1224(m), 1145(vs, broad), 1031(m), 1012(w), 960(w), 945(m), 919(w), 889(w), 849(m), 788(m), 765(m), 720(w), 690(w) cm^{-1} .

Oxidation of π -Mesitylene- π -[exo-6-(4-hydroxy-2,6-di-*tert*-butylphenyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate

Solutions of π -mesitylene- π -[exo-6-(4-hydroxy-2,6-di-*tert*-butylphenyl)-1,3,5-trimethylcyclohexadienyl]iron(II) hexafluorophosphate (90 mg, 0.14 mmol) in 20 ml of CH_2Cl_2 and ammonium hexanitratocerate(IV) (1.0 g, 1.8 mmol) in 20 ml of water were shaken together in a separatory funnel until the organic layer was almost colorless. The organic layer was separated, and the aqueous layer was washed with 25 ml of CH_2Cl_2 . The combined CH_2Cl_2 layers were dried over MgSO_4 , filtered, and evaporated. Only a very small amount of a dark green oil remained. An NMR spectrum indicated that if the expected product, 3,5-di-*tert*-butyl-4-hydroxy-2',4',6'-trimethylbiphenyl (15), was present, it was part of a mixture, perhaps not even a major part. The NMR spectrum was as follows (τ , CCl_4): 3.12 (broad s,1), 3.58(s,1), 7.69 and 7.75(overlapping s, ca. 4), 8.49 (s,2.5), 8.71(s, ca. 4), 8.88(broad s, ca. 1).

Attempted Synthesis of Bis(π -exo-6-cyano-1,3,5-trimethylcyclohexadienyl)iron(II)

A. KCN (26 mg, 0.39 mmol) and 2,5,8,15,18,21-hexaoxa-[20.4.0.0⁹,1⁴]hexacosane (dicyclohexyl-18-crown-6) (149 mg, 0.40 mmol) were stirred together in 30 ml of acetone. All but a very little of the KCN dissolved. This solution was added dropwise to a stirred solution of π -mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate (187 mg, 0.40 mmol) in 20 ml of acetone. A very finely divided solid immediately began forming. After two minutes the reaction mixture was filtered through a medium-porosity filter, which caught the few remaining crystals of KCN but allowed the finely divided solid to pass through. Filtration through a fine-porosity filter gave an orange solution and a shiny black solid whose IR spectrum (KBr pellet) showed two distinct C \equiv N absorptions (2055 and 2200 cm⁻¹). Evaporation of the solution gave an orange solid which was soluble in CH₂Cl₂ but did not color diethyl ether and was assumed to be unreacted starting material. There was no evidence of formation of the desired product.

B. KCN (29 mg, 0.44 mmol) was dissolved in a solution of dicyclohexyl-18-crown-6 (170 mg, 0.45 mmol) in 40 ml of nitromethane. This solution was added dropwise to a stirred solution of π -mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate (210 mg, 0.45 mmol) in a small amount of nitromethane. Almost immediately the solution took on an orange-green appearance similar to that of fluorescein solutions. After 20 minutes of stirring, the solution was filtered through a fine-porosity filter. Removal of the solvent left a green-brown oil which was insoluble in both pentane

and diethyl ether. Addition of CH_2Cl_2 gave an orange solution and a very small amount of a deep blue solid. The orange, CH_2Cl_2 -soluble material was precipitated by addition of diethyl ether and was presumed to be unreacted starting material. There was no evidence of the desired product.

C. Bis(mesitylene)iron(II) hexafluorophosphate (590 mg, 1.0 mmol), KCN (260 mg, 4.0 mmol), and 1,4,7,10,13,16-hexaoxacyclooct-decane (18-crown-6) (30 mg, 0.1 mmol) were added to 50 ml of dry benzene. The reaction flask was fitted with a reflux condenser and a CaSO_4 drying tube, but no effort was made to exclude oxygen. The mixture was refluxed for 19 hours. When the mixture was allowed to cool to room temperature and the stirring was stopped, all the colored material settled out, and no color remained in the solution. The benzene was evaporated, and the solid was extracted with CCl_4 . An NMR spectrum of this extract showed no absorptions except added TMS. When the residue was extracted with CH_2Cl_2 , an orange solution resulted. The orange material was easily precipitated with diethyl ether. The resulting orange solid was collected, washed with ether, and dried under vacuum for 15 minutes. This material was identified as π -mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate by comparison with a known sample. The yield was 270 mg (58%).

Attempted Synthesis of Bis(π -exo-6-nitromethyl-1,3,5-trimethylcyclohexadienyl)iron(II)

A. Potassium tert-butoxide (450 mg, 4.0 mmol) was stirred with 35 ml of nitromethane. Not all of the solid dissolved, but some of

it obviously did. A solution of bis(mesitylene)iron(II) hexafluorophosphate (590 mg, 1.0 mmol) in five ml of nitromethane was added, and the color changed to deep red almost immediately and in spite of dilution. After ca. two minutes of stirring, 18-crown-6 (50 mg, 2 mmol) was added. Some more of the alkoxide appeared to dissolve, and the solution became somewhat darker and browner. After 15 minutes, dark solid became evident, so the reactants were precipitated by pouring the reaction mixture into 400 ml of technical grade diethyl ether. No color remained in solution. The solids were collected and dried. Extraction with CH_2Cl_2 gave an orange solution, but some insoluble orange material remained. All of the CH_2Cl_2 -insoluble material was soluble in acetone.

B. Potassium tert-butoxide (450 mg, 4.0 mmol), 18-crown-6 (30 mg, 0.1 mmol), and nitromethane (240 mg, 4.0 mmol) were stirred together with 50 ml of dry benzene. Bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) was added, and the benzene was refluxed for 17 hours with continuous stirring. The reaction mixture was allowed to cool to room temperature, and stirring was terminated. A red-brown solid settled, leaving no color in solution. Since no di-adduct of the type 16 has been reported insoluble in nonpolar solvents, it was assumed that the desired product was not present. The solid was separated by filtration, and the benzene was evaporated on a rotary evaporator to give a colorless oil. An NMR spectrum of this oil in CCl_4 showed no sign of 2-nitromethyl-1,3,5-trimethylbenzene.

Attempted Synthesis of Bis[π -exo-6-(1-nitroethyl)-1,3,5-trimethylcyclohexadienyl]iron(II)

Bis(mesitylene)iron(II) hexafluorophosphate (586 mg, 1.0 mmol) and lithium methoxide (150 mg, 4.0 mmol) were stirred together in 40 ml of nitroethane at 60°. Since the iron complex dissolves only slowly in nitroethane, no immediate reaction was observed. After 30 minutes the solution began to darken rather suddenly. After 45 minutes the reaction mixture was cooled to room temperature. Neither unreacted starting material nor nucleophilic addition product thereof could be isolated.

Anomalous Decomposition of Bis(mesitylene)iron(II) Hexafluorophosphate in the Presence of Nucleophiles and Absence of Oxygen

A. Potassium Cyanide

Solid KCN (0.33 g, 5.0 mmol) was added to a stirred, partially dissolved suspension of bis(mesitylene)iron(II) hexafluorophosphate (1.17 g, 2.0 mmol) in 100 ml of acetone under nitrogen. For the first ten minutes of stirring, there was no observable change except darkening of the KCN crystals. Then, the remaining solid iron complex quite suddenly dissolved, and the solution turned from a medium orange to light yellow in a few seconds. Extension of the reaction time to 75 minutes resulted in a greenish solution. In no case was any detectable amount of the expected product formed under nitrogen.

In a separate experiment it was found that the mono-adduct (6, R = CN) was not similarly decomposed by stirring in acetone under nitrogen either in the presence or absence of KCN.

B. Sodium Azide

Solid NaN_3 (0.13 g, 2.0 mmol) was added to a stirred, partially dissolved suspension of bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) in 50 ml of acetone under nitrogen. The solution was instantly decolorized, and no further color appeared. The solid iron complex gradually disappeared, apparently decomposing as soon as it dissolved. No identifiable organoiron compounds were isolated from this reaction.

C. Lithium Amide

Solid LiNH_2 (79 mg, 3.0 mmol) and solid bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) were stirred together under nitrogen in 50 ml of dry THF. The reaction mixture slowly darkened with continued stirring until, after one hour, it was almost black. There was no color in the solution. When the reaction was run in dry diethyl ether, under either nitrogen or argon, the mixture darkened more slowly, but the eventual result was the same.

D. Potassium Cyanate

Bis(mesitylene)iron(II) hexafluorophosphate (0.59 g, 1.0 mmol) was stirred with a large molar excess of KOCN in 50 ml of acetone under nitrogen. After ten minutes of stirring, no orange color remained either in solution or as a solid.

Behavior of π -Mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) Hexafluorophosphate Under Vacuum

When π -mesitylene- π -exo-6-cyano-1,3,5-trimethylcyclohexadienyliron(II) hexafluorophosphate was evacuated overnight in a dessicator, it turned from orange to gray. Extraction of the undecomposed

material with CH_2Cl_2 left a royal blue solid which was insoluble in CCl_4 , CHCl_3 , CS_2 , benzene, acetone, and water. The IR spectrum of this material (KBr pellet) exhibited an intense peak at 2075 cm^{-1} , clearly indicating the presence of inorganic cyanide. Addition of pyridine gave a deep reddish-brown solution. Reprecipitation with diethyl ether gave a brown solid whose IR spectrum contained no $\text{C}\equiv\text{N}$ stretch. Therefore, the blue solid appears to be insoluble in solvents which do not decompose it.

Preparation of Bis(pentamethylbenzene)iron(II) Hexafluorophosphate
from $\text{Fe}(\text{CO})_4\text{I}_2$

All operations in this experiment prior to the hydrolysis step were performed under nitrogen. $\text{Fe}(\text{CO})_4\text{I}_2$ was prepared from $\text{Fe}(\text{CO})_5$ and iodine by a slight modification of the reported synthesis.⁴³ A solution of iodine (5.08 g, 20 mmol) in 40 ml of ether was slowly added to a stirred solution of $\text{Fe}(\text{CO})_5$ (2.9 ml, 21 mmol) in 10 ml of diethyl ether. Vigorous bubbling, presumably the evolution of carbon monoxide, accompanied this addition. When the addition was complete, the solution was blown almost to dryness with a stream of nitrogen. The resulting crystals of $\text{Fe}(\text{CO})_4\text{I}_2$ were placed on a filter, washed with petroleum ether, and sucked dry to yield 7.69 g (91%).

$\text{Fe}(\text{CO})_4\text{I}_2$ (7.69 g, 18.2 mmol) was placed in a three-neck, round-bottom flask and covered with a little petroleum ether. Solid AlCl_3 (4.85 g, 36.4 mmol) and a solution of pentamethylbenzene (5.40 g, 36.4 mmol) in petroleum ether were added. The mixture was stirred mechanically for 24 hours, then cooled to 0° and hydrolyzed by addition of 100 ml of 5% methanol in water. The resulting mixture was filtered and separated, and the aqueous layer was washed with 30

ml of petroleum ether. Addition to the aqueous layer of a solution of NH_4PF_6 (6.52 g, 40 mmol) in 10 ml of water caused the precipitation of an orange solid. This material, bis(pentamethylbenzene)iron(II) hexafluorophosphate, was collected on a filter and dried by evacuation for 24 hours to give 0.41 g (3.5%). The organic ligands were obtained by treating an acetone solution of the iron complex with concentrated aqueous NaOH and extracting the resulting mixture with pentane. Gas chromatography showed the organic portion to consist of 98% pentamethylbenzene and 2% durene. No hexamethylbenzene was detected.

^1H NMR spectrum (τ , acetone- d_6): 3.30(s,1), 7.44, 7.46, and 7.52 (overlapping singlets, combined area 15).

Preparation of Bis(durene)iron(II) Hexafluorophosphate from $\text{Fe}(\text{CO})_4\text{I}_2$

$\text{Fe}(\text{CO})_4\text{I}_2$ (6.61 g, 15.7 mmol), AlCl_3 (4.17 g, 31.4 mmol), and durene (4.22 g, 31.4 mmol) were stirred together under nitrogen in petroleum ether for 24 hours. The mixture was cooled to 0° and hydrolyzed with 100 ml of 5% methanol in water and filtered. The aqueous layer was washed with petroleum ether and treated with a solution of NH_4PF_6 (13.04 g, 80 mmol) in water to precipitate the orange product, bis(durene)iron(II) hexafluorophosphate. Drying overnight under vacuum left 0.88 g of product (9.1%). The organic ligands were obtained as in the preceding procedure. Gas chromatography indicated that the organic portion was 98% durene and 2% pentamethylbenzene. No trimethylbenzenes were detected.

^1H NMR spectrum (τ , acetone- d_6): 3.10(s,1), 7.35(s,6).

Attempted Preparation of Bis(durene)iron(II) Hexafluorophosphate from $\text{Fe}(\text{CO})_4\text{Br}_2$

$\text{Fe}(\text{CO})_4\text{I}_2$ was generated in situ by adding dropwise a solution

of Br_2 (3.20 g, 20 mmol) in 15 ml of petroleum ether to a stirred solution of $\text{Fe}(\text{CO})_5$ in 10 ml of petroleum ether at 0° . A great deal of gas was evolved during the addition, and a brown solid formed.

A solution of durene (5.51 g, 41 mmol) in petroleum ether and solid AlCl_3 (7.0 g, 52.5 mmol) were added to the prepared $\text{Fe}(\text{CO})_4\text{Br}_2$,⁴³ and the mixture was stirred mechanically for three hours. The reaction flask was then cooled to 0° again, and 75 ml of 5% methanol in ice and water were added. After having been stirred for 20 minutes, the mixture was filtered, and the aqueous phase was washed twice with petroleum ether. When a solution of NH_4PF_6 (19.6 g, 120 mmol) in water was added, only a small amount of solid suspension formed.

Reactions of Bis(arene)iron(II) Bromides with D_2O in the Presence of Organic Bases

A. Hexamethylbenzene

When bis(hexamethylbenzene)iron(II) bromide was dissolved in D_2O in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane, all protons of the iron complex exchanged with the solvent. NMR spectroscopy indicated that the exchange was 75% complete after 90 minutes at room temperature and 94% complete after 24 hours. This was confirmed by mass spectral measurements of the deuterated iron complex, which had been precipitated with acetone and dried under vacuum.

Uncoordinated hexamethylbenzene underwent no exchange detectable by mass spectrometry after 20 hours in 5% D_2O /95% DMF at room temperature in the presence of the same catalyst.

B. Partially Methylated Benzenes

When Procedure A was repeated using other bis(arene)iron(II)

bromides, specifically those with pentamethylbenzene, durene, or mesitylene as ligands, no observable exchange occurred. Instead, decomposition of the complexes occurred almost immediately, as evidenced by the formation of green precipitates. Use of s-collidine as the catalyst with bis(durene)iron(II) bromide gave the same result. Use of sodium acetate as the catalyst with bis(mesitylene)iron(II) bromide gave a white precipitate, which began forming after ca. 10 minutes.

When "proton sponge" (1,8-bis(dimethylamino)naphthalene), a supposedly nonnucleophilic base, was used as the catalyst with bis-(durene)iron(II) bromide, neither exchange nor decomposition was observed. This was probably due to the low solubility of proton sponge in D₂O. Mixing acetone solutions of proton sponge and bis-(durene)iron(II) hexafluorophosphate resulted in almost immediate decomposition of the complex.

Attempted Trapping of "Bis(6-methylene-2,4-dimethylcyclohexadienyl)-iron(II)" with Benzaldehyde

NaN[Si(CH₃)₃]₂ (2.10 g, 11.5 mmol) was added to a solution consisting of 25 ml of benzene and 25 ml of benzaldehyde. Some heat was evolved, and the solution became viscous. Bis(mesitylene)iron(II) hexafluorophosphate (590 mg, 1.0 mmol) was added, and the mixture was subjected to vigorous mechanical stirring for 15 minutes. A small amount of white solid was removed by filtration, and what remained was heated and evacuated to remove benzene and unreacted benzaldehyde. No starting material was recovered. What remained was chromatographed through silica gel made up with hexane and eluted with hexane, benzene, diethyl ether, and CH₂Cl₂, in that order. The effluent was monitored

by NMR. At least six or seven products were present, none of which was completely separated by the silica gel chromatography. The NMR spectra of the early fractions showed (among others) peaks characteristic of benzyl benzoate (vide infra).

Attempted Preparation and Purification of Bis(methylenepentamethylcyclohexadienyl)iron(II)

A. Chromatography

Bis(hexamethylbenzene)iron(II) bromide² (480 mg, 1.2 mmol) and $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ (520 mg, 2.8 mmol) were added to 50 ml of dry diethyl ether under nitrogen and stirred. Substantial color entered the solution after a few minutes. After one hour the reaction mixture was filtered under nitrogen to give an orange solution and a dark brown solid. The solution was blown dry with nitrogen, and the residue was dried under vacuum. The dry residue, which appeared to be a mixture of white crystals contaminated with an orange solid, was dissolved in hexane and poured onto a column of neutral alumina prepared in hexane. Elution with hexane caused hexamethylbenzene to come off the column, but neither hexane, hexane/benzene, benzene nor diethyl ether moved the colored material.

This experiment was repeated using silica gel in place of alumina. In this case, the reaction mixture was not filtered, but simply blown dry, shaken with hexane, and poured onto the column. Elution with hexane caused some colored material to enter the silica gel, but this appeared to decompose on the column. At one point the colored material on the column took on a distinctly purple color. Changing the eluent to benzene caused more colored material to start down the column, but again none could be eluted. Changing the

eluent to diethyl ether produced no more movement of colored material.

B. Sublimation

Bis(hexamethylbenzene)iron(II) bromide² (150 mg, 0.38 mmol) and $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ (340 mg, 1.85 mmol) were ground together in the bottom of a small sublimator. The iron complex could be seen to darken almost immediately. The sublimator was assembled, evacuated to 0.05 torr, and heated to 130° for three hours. The white crystals which collected on the cold finger were identified as hexamethylbenzene (a single NMR peak); no evidence for the presence of other compounds in the sublimate was found.

In another experiment 1.3 mmol (540 mg) of bis(hexamethylbenzene)iron(II) bromide was treated with 1.6 mmol (300 mg) of $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ in diethyl ether. The reaction mixture was filtered and blown dry as in Procedure A. The residue was subjected to room-temperature sublimation for four days with the cold finger maintained at -78°. The sublimate consisted entirely of hexamethylbenzene, which was again identified by NMR. The colored material, which remained unsublimed, did not color benzene and was, therefore, assumed to have decomposed.

C. Direct Isolation

Several attempts to obtain an NMR spectrum of the reaction product of base with bis(hexamethylbenzene)iron(II) bromide failed because of decomposition of that product. Finally, bis(hexamethylbenzene)iron(II) bromide² (540 mg, 1.0 mmol) and potassium tert-butoxide (340 mg, 4.0 mmol) were stirred together in 50 ml of dry

diethyl ether under nitrogen for two hours. The reaction mixture was filtered in a dry box to give a deep red-brown solution. This solution was removed from the dry box and evaporated to dryness at room temperature with a vacuum pump. The dry residue was returned to the dry box and taken up in benzene- d_6 . The resulting orange solution was filtered into an NMR tube, and the tube was sealed with Teflon tape. The NMR spectrum exhibited a very large peak for hexamethylbenzene and several small peaks (τ 6.71, 6.94, 7.11, 7.61, 8.03, and 8.80) which could not be correlated with the proposed structure and for which no other structure seemed appropriate either. The solution showed no sign of decomposition in the NMR machine.

Attempted Trapping of "Bis(methylenepentamethylcyclohexadienyl)iron(II)"

A. Methyl Iodide

Bis(hexamethylbenzene)iron(II) bromide² (540 mg, 1.0 mmol) and $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ (500 mg, 2.7 mmol) were stirred together in 50 ml of dry diethyl ether under nitrogen. After ten minutes the reaction mixture was filtered to give an orange solution. This solution was combined with a solution of CH_3I (1.25 ml, 2.0 mmol) in 10 ml of dry ether. No immediate change was observed. After the solution had stirred overnight, a white precipitate had formed, and most of the color had disappeared. There was no sign of the expected product, bis(ethylpentamethylbenzene)iron(II) iodide, which should have been a brilliant red solid by analogy with other bis(arene)iron(II) iodides. The ether was evaporated, and the residue was shaken with CCl_4 and filtered. An NMR spectrum of this solution showed only hexamethylbenzene and no ethylpentamethylbenzene.

B. Benzaldehyde

Bis(hexamethylbenzene)iron(II) hexafluorophosphate dihydrate² (0.71 g, 1.0 mmol) was dissolved in 30 ml of acetone to give a bright red solution. A catalytic amount of 1,4-diazabicyclo[2.2.2]-octane was added, and the solution darkened as it dissolved. When the amine had dissolved completely, a large molar excess of benzaldehyde was added. No immediate change was observed. After 24 hours the starting compound was recovered unchanged.

C. Iodine Monochloride

Bis(hexamethylbenzene)iron(II) bromide² (540 mg, 1.0 mmol) and $\text{KOC}(\text{CH}_3)_3$ (340 mg, 3.0 mmol) were stirred together in 50 ml of dry diethyl ether under nitrogen for 18 hours. Filtration under nitrogen gave a deep red-brown solution. Iodine monochloride (0.32 g, 2.0 mmol) was dissolved in 10 ml of dry ether and added. An orange precipitate formed immediately and quickly settled. Enough unreacted ICl was left to color the solution. The solid was collected on a filter and washed with ether. This solid did not exhibit the properties expected for the proposed product. Specifically, it was somewhat soluble in acetone, although not soluble enough to get an NMR. Furthermore, its mass spectrum exhibited a very large peak for the hexamethylbenzene parent ion (m/e 162), but a peak only a little above noise level for the expected iodo derivative ($\text{C}_{12}\text{H}_{17}\text{I}^+$, m/e 288).

D. Deuterium Chloride

By starting with 540 mg (1.0 mmol) of bis(hexamethylbenzene)iron(II) bromide,² a deep red-brown ethereal solution of "bis(methylene-

pentamethylcyclohexadienyl)iron(II)" was obtained as in Procedure C. This was shaken with a solution obtained by bubbling HCl through ca. 10 ml of D₂O. After five minutes most of the color had left the organic phase and entered the aqueous phase. The phases were separated, and the aqueous phase was treated with a solution of NH₄PF₆ (0.82 g, 5.0 mmol) in a minimum amount of water. An orange precipitate formed immediately. The mass spectrum of this material showed no detectable deuteration of hexamethylbenzene, and the IR spectrum exhibited no obvious C-D stretch.

E. Acetyl Chloride

Procedure C was repeated using the same amount of iron complex and acetyl chloride (165 mg, 2.1 mmol) in place of ICl. Only 0.5 g (3.0 mmol) of NH₄PF₆ was used. The orange solid obtained was definitely not the expected product, bis(pentamethylphenylacetone)iron(II) hexafluorophosphate. The IR spectrum showed no ketone carbonyl absorption. The NMR spectrum in acetone-d₆ was a confusion of small peaks that did not suggest a pure compound. The mass spectrum exhibited no peak at m/e 204 (pentamethylphenylacetone parent ion), but the second largest peak in the spectrum was at m/e 162 (hexamethylbenzene parent ion).

F. Bromine

Procedure C was repeated using the same amounts of materials but using bromine (1.5 ml, 3.0 mmol) in place of ICl. When the bromine was added, a bright yellow, water-insoluble precipitate formed. A mass spectrum of this material exhibited fragment patterns attributable to C₁₂H_{18-n}Br_n⁺ for n = 0 to 5 with intensity decreasing as n increased.

G. Simmons-Smith Reagent

All steps in this procedure were performed under nitrogen. CH_2I_2 (0.54 g, 2.0 mmol) was dissolved in a few milliliters of dry diethyl ether which contained a catalytic amount of iodine. The resulting solution was added to a stirred suspension of zinc-copper couple⁴⁴ (0.16 g, 2.5 mmol) in 15 ml of dry ether and refluxed for 15 minutes.

A deep red-brown ethereal solution of "bis(methylenepentamethylcyclohexadienyl)iron(II)" was generated as in Procedure C (same amounts of materials). This solution was added dropwise to the stirred suspension described in the preceding paragraph without refluxing. Each drop was decolorized almost instantly. A substantial amount of fluffy, gray solid formed as the addition progressed. When the stirrer was turned off, all the solid quickly settled, leaving a colorless solution.

Unsuccessful Attempted Nucleophilic Additions to Bis(mesitylene)-iron(II) Hexafluorophosphate Exposed to Air

A. Thiocyanate

Bis(mesitylene)iron(II) hexafluorophosphate (293 mg, 0.5 mmol) was stirred in 50 ml of acetone until it dissolved. When KSCN (49 mg, 0.5 mmol) was added, the solution immediately changed from orange to bright red. Filtration and removal of the acetone left a brick-red residue. An NMR spectrum of this residue in acetone- d_6 showed no absorptions except those of TMS (internal standard) and the acetone- d_5 impurity. The residue was, therefore, considered to be inorganic and not the expected product (6, $\text{R}' = \text{SCN}$).

B. Thiophenoxide

Lithium methoxide (57 mg, 1.5 mmol) and thiophenol (2.0 ml, 2.0 mmol) were dissolved in 50 ml of dry methanol. Bis(mesitylene)-iron(II) hexafluorophosphate (590 mg, 1.0 mmol) was added, and the reaction mixture immediately turned black. After two hours the methanol was evaporated, and a reddish oil remained. This oil was extracted with CH_2Cl_2 , and an NMR spectrum of the extract evidenced only thiophenol, thiophenoxide, and mesitylene.

In a separate experiment, solid potassium thiophenoxide was used as the source of thiophenoxide, and the reaction solvent was THF. Again, the reaction mixture turned black as soon as the iron complex was added. Filtration gave a red-brown THF solution, but after the colored material had been precipitated with diethyl ether it would not redissolve in THF. Since compounds of the type 6 are soluble in THF, it was assumed that this was not the desired product.

C. Cyanate

Bis(mesitylene)iron(II) hexafluorophosphate (590 mg, 1.0 mmol) and a large excess of KOCN were stirred together for one hour in 50 ml of acetone. When the acetone was evaporated and the residue stirred with CH_2Cl_2 , almost no colored material entered the solution.

D. Phenoxide

Lithium methoxide (0.30 g, 3.0 mmol) and bis(mesitylene)iron(II) hexafluorophosphate (1.47 g, 2.5 mmol) were stirred together in 100 ml of dry THF for 48 hours. Evaporation of the solvent left a chocolate brown residue which dispersed into CH_2Cl_2 but did not form a true solution.

E. Acetate

Bis(mesitylene)iron(II) hexafluorophosphate (590 mg, 1.0 mmol) was dissolved in 12 ml of DMF. When solid sodium acetate trihydrate (270 mg, 2.0 mmol) was added, the solution quickly changed from orange to dark red to black. Addition of 50 ml of diethyl ether gave a precipitate which had a pronounced tendency to revert to an oil. The oil could be resolidified by decanting the supernatant liquid, redissolving the oil in a few milliliters of DMF, and reprecipitating with ether. In this way enough brown solid was obtained to be collected on a filter. This material was washed through the filter with CH_2Cl_2 , but in that solution it underwent rapid decomposition, evidenced by the appearance of suspended solid. The brown color and instability in CH_2Cl_2 suggested that this material was not the desired product (6, $\text{R} = \text{OCOCH}_3$).

F. Fluoride

Bis(mesitylene)iron(II) hexafluorophosphate (590 mg, 1.0 mmol) was dissolved in a small volume of $[(\text{CH}_3)_2\text{N}]_3\text{PO}$. A large excess of potassium fluoride was added, and the reaction mixture was swirled for five minutes. Diethyl ether (100 ml) was added, and the resulting solid was filtered and extracted with CH_2Cl_2 . Only a very faint color entered the CH_2Cl_2 solution, but when this solution was treated with diethyl ether, a copious white precipitate formed. In a similar experiment run without the iron complex, no precipitate formed. The dry weight of this precipitate was 0.72 g. Its mass spectrum was almost identical to that of $[(\text{CH}_3)_2\text{N}]_3\text{PO}$ except for a large peak at m/e 107.

When this experiment was repeated with DMF as the solvent,

essentially the same result was obtained, except that in this case the white precipitate rapidly decomposed on exposure to air to a brown, gummy solid which was insoluble in CH_2Cl_2 .

Attempted Reaction of Bis(hexamethylbenzene)iron(II) Bromide with Sodium Hydride

Bis(hexamethylbenzene)iron(II) bromide (540 mg, 1.0 mmol) was stirred for three hours with a large excess of sodium hydride in 60 ml of dry diethyl ether. A substantial amount of color appeared to enter the solution, but when the reaction mixture was filtered rapidly under nitrogen, the solution was almost colorless. Three subsequent repetitions of this reaction gave no colored ether solutions.

Thermal Decomposition of Bis(mesitylene)iron(II) Iodide

Bis(mesitylene)iron(II) iodide (0.55 g, 1.0 mmol) was evacuated to 0.05 torr and decomposed by heating with a heat gun. The volatile products were collected in a dry ice-acetone cold trap. An NMR spectrum in CCl_4 of the liquid collected showed it to be entirely mesitylene with no detectable amounts of iodomesitylene or other products.

Thermal Stability of π -Mesitylene- π -[exo-6-(1-nitroethyl)-1,3,5-trimethylcyclohexadienyl]iron(II) Hexafluorophosphate in Nitroethane

When a solution of π -mesitylene- π -[exo-6-(1-nitroethyl)-1,3,5-trimethylcyclohexadienyl]iron(II) hexafluorophosphate in nitroethane was heated slowly, no change was observed up to ca. 70°. Between 70° and 90° there was some darkening of the solution, but no solid formed. Between 90° and 95° there was a fairly sharp transition in which all the color left the solution as a red-brown precipitate.

Attempted Synthesis of Bis(mesitylene)cobalt(III) Hexafluorophosphate from Tris(acetylacetonato)cobalt(III)

Tris(acetylacetonato)cobalt(III) (3.56 g, 10 mmol), AlCl_3 (10.66 g, 80 mmol), mesitylene (3.61 g, 30 mmol), and cyclohexane (50 ml) were combined in a dry, three-neck, round-bottom flask. The mixture was heated to reflux and stirred mechanically for three hours. No evolution of HCl was observed, but a red-brown solid formed. The mixture was cooled to -10° and hydrolyzed by slow addition of ice. Hydrolysis was accompanied by complete disappearance of the red-brown color. After the ice had melted, the aqueous layer had a pink color typical of inorganic cobalt(II). When concentrated aqueous NH_4PF_6 was added, no precipitate formed. When the experiment was repeated and the mixture was cooled in dry ice-acetone before hydrolysis, the same result was obtained.

Attempted Synthesis of Bis(6-oxo-1,5-di-tert-butylcyclohexadienyl)iron(II)

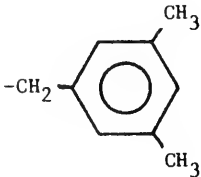
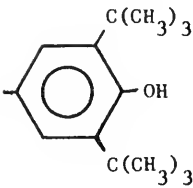
FeCl_2 (0.25 g, 2.0 mmol) and potassium 2,6-di-tert-butylphenoxide (0.97 g, 2.0 mmol) were stirred together in 100 ml of dry diethyl ether for 24 hours. A dark brown solid formed which was insoluble in both diethyl ether and acetone. There was no evidence of the desired product.

Isolation of Benzyl Benzoate from the Reaction of Benzaldehyde and Sodium Bis(trimethylsilyl)amide

$\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ (0.84 g, 4.6 mmol) was added to a mixture of 25 ml of dry benzene, 10 ml of benzaldehyde, and 0.12 g of mesitylene under nitrogen. The mixture was stirred magnetically for 18 hours, diluted with 50 ml of technical grade acetone, and filtered. A gummy, white solid and a yellowish liquid resulted. The yellow liquid was

heated and evacuated to remove benzene, benzaldehyde, mesitylene, and other relatively low-boiling materials. The yellow oil that remained was chromatographed through 12 inches of silica gel prepared in hexane. The first compound eluted was also by far the most abundant. It was identified as benzyl benzoate by NMR, IR, and mass spectrometry. The yield of this product was 3.65 g (17.2 mmol, 374% based upon the amide). The other components, none of which was present in large amount, were not characterized.

TABLE I
MELTING POINTS OF THE MONO-ADDUCTS (6)

<u>R</u>	<u>Melting point (°)</u>
-CN	90 (a)
-CH ₂ NO ₂	165 (a)
-CH(CH ₃)NO ₂	135 (a)
	168-70
	239 (a)
-CH ₂ COOC(CH ₃) ₃	194-5 (b)

(a) decomposes without melting

(b) melts with decomposition

TABLE II
ELEMENTAL ANALYSES OF THE MONO-ADDUCTS (6)

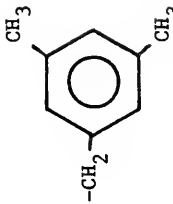
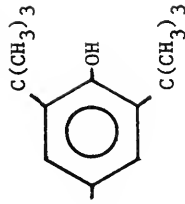
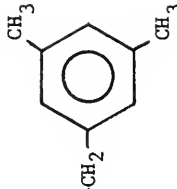
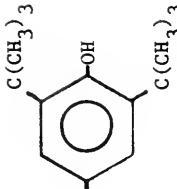
<u>R</u>	<u>Formula</u>	<u>%C</u>	<u>Calculated</u> <u>%H</u>	<u>%N</u>	<u>Found</u> <u>%H</u>	<u>%N</u>
-CN		48.84	5.18	3.00	48.86	2.76
-CH ₂ NO ₂		45.52	5.23	2.80	45.38	3.04
-CH(CH ₃)NO ₂		46.62	5.48	2.72	46.20	2.92
		57.87	6.30	----	58.35	6.26
		59.45	7.02	----	60.04	7.73
-CH ₂ COOC(CH ₃) ₃		49.29	6.06	----	51.81	6.34

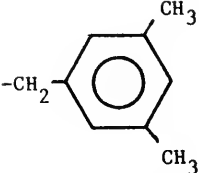
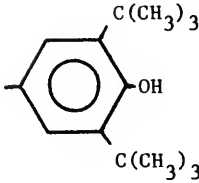
TABLE III
UV-VISIBLE SPECTRA OF THE MONO-ADDUCTS (6) IN METHANOL

<u>R</u>	<u>Absorptions(nm), $\lambda(\epsilon)$</u>	
-CN	220(19000) 241(17300)	294(3990) 339(1820) 406(435)
-CH ₂ NO ₂	217(20200) 241(17800)	297(4200) 340(2190) 406(528)
-CH(CH ₃)NO ₂	218(19200) 242(17800)	297(4250) 340(2330) 402(464)
	(a) 237(21900)	290(5400) 350(2750) 403(541)
	213(28000) 247(24800)	292sh(6730) 350(3100) 405sh(505)
-CH ₂ COOC(CH ₃) ₃	214(22400) 229(22600)	286(5050) 349(2600) 408(546)

(a) peak obscured by strong end absorption

TABLE IV

SELECTED MASS-SPECTRAL DATA OF THE MONO-ADDUCTS (6) (a)

<u>R</u>	$\frac{(C_9H_{11}R)^+}{m/e \quad \%}$		$\frac{M^+}{m/e \quad \%}$	
	<u>m/e</u>	<u>%</u>	<u>m/e</u>	<u>%</u>
-CN	145	(b)	467	(b)
-CH ₂ NO ₂	179	0.5	501	(b)
-CH(CH ₃)NO ₂	193	(b)	515	(b)
	238	0.3	560	(b)
	324	37	646	1.2
-CH ₂ COOC(CH ₃) ₃	234	(b)	556	(b)

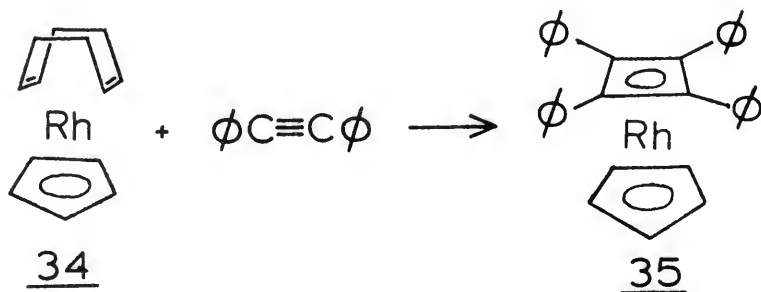
- (a) in each case the base peak occurred at m/e 105 (mesitylene minus methyl), the peak next in size occurred at m/e 120 (mesitylene)
 (b) not observed

II. SYNTHESIS AND STRUCTURE OF π -CYCLOPENTADIENYL- π -TETRA-PHENYLCYCLOBUTADIENERHODIUM(I)

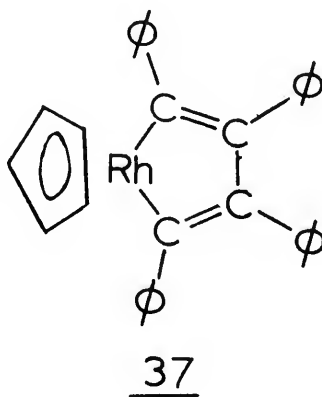
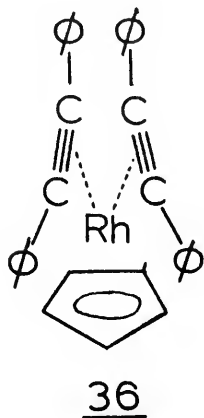
INTRODUCTION

Several routes to cyclobutadiene complexes of cobalt appear in the literature, namely, the following: (1) the reaction of dicyclopentadienylcobalt(II), π -cyclopentadienyl- π -1,5-cyclooctadienecobalt(I), or π -cyclopentadienyldicarbonylcobalt(I) with internal acetylenes,^{4,5} (2) by the irradiation of π -cyclopentadienyldicarbonylcobalt(I) with α -pyrone,^{4,6} (3) by a multistep synthesis starting with 3,4-dichlorobutene,^{4,7} and (4) by ligand-transfer reactions.^{4,8} At the time the present work was performed, however, there was no report in the literature of an analogous complex of rhodium. The work described here led to the first report of such a complex.^{4,9} Other workers have since published syntheses of additional cyclobutadiene-rhodium complexes.^{50,51}

Reaction of π -cyclopentadienyl- π -1,5-cyclooctadienerrhodium(I) with diphenylacetylene at 180° for 48 hours gave π -cyclopentadienyl-



π -tetraphenylcyclobutadienerhodium(I) in consistently low yield, usually less than 1%. The limited availability of this material made chemical characterization difficult. It was not clearly demonstrable, for example, that what had formed was a true cyclobutadiene complex and not the isomeric bis(acetylene)rhodium (36) or rhodacyclopentadiene (37). For this reason, an X-ray crystallographic study was undertaken. Some time after the results of this study were published, other workers reported a high-yield synthesis of the complex by a different route starting with bis(trifluorophosphine)rhodium(I) dimer.⁵¹



SYNTHESIS AND SPECTRA

The yellow, air-stable, crystalline compound π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I), 38, was synthesized by allowing π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) to react with a large excess of diphenylacetylene at 180° under nitrogen for 48 hours. The major product of this reaction was hexaphenylbenzene, and the yields of 38 were consistently low. The use of toluene as a solvent did not improve the yield but only increased the difficulty of isolating 38. There was no evidence of more than one chromatographable product from this reaction. Rausch *et al.*⁵² reported that reaction of π -cyclopentadienyldicarbonylrhodium(I) with diphenylacetylene in refluxing toluene gave, in addition to several other products, a complex of the formula $C_5H_5Rh(C_2\phi)_2 \cdot C_6H_5CH_3$. They did not propose a structure for this complex, but claimed that the toluene was chemically bound and not simply solvent of crystallization. The compound did, however, lose the elements of toluene from the molecular ion in the mass spectrometer to give $C_5H_5Rh(C_2\phi)_2^+$, m/e 524.

The complex 38 exhibited some interesting and unexpected spectral properties. There is a marked solvent effect on the phenyl proton resonances in the NMR spectrum. In CS_2 these resonances appear as a single multiplet centered at 2.9τ . In C_6D_6 , however, two multiplets of relative areas 2:3 appear at 2.4τ and 2.9τ , re-

spectively. Other tetraphenylcyclobutadiene-transition metal complexes exhibit either one or two multiplets in the phenyl region,⁴⁸ but there has apparently been no case reported in which a single complex displayed both patterns as a result of solvent change. In both media the cyclopentadienyl protons appear as a doublet with a separation of 1.1 Hz. Since this separation is the same in both the 60-MHz and 100-MHz spectra, it is clearly due to ^{103}Rh - ^1H coupling and not to nonequivalence of the protons. (The ^{103}Rh isotope, $I = \frac{1}{2}$, is 100% abundant in nature.)

This phenomenon is observed in a few other organorhodium compounds,^{50, 52-4} but in others which are seemingly similar it is not.^{55, 56} There is, for example, no evidence of such coupling in π -cyclopentadienyl- π -1,5-cyclooctadienylrhodium(I), the immediate precursor of 38. A section on metal-hydrogen coupling in a recent review article⁵⁷ does not mention rhodium at all. In all complexes of rhodium with delocalized hydrocarbon anions for which $^2J(^{103}\text{Rh}-^1\text{H})$ is reported, it is less than 2.0 Hz. Although a theoretical treatment of coupling is beyond the scope of this dissertation, two experimental phenomena reported by various workers may be invoked to account for these small values. First, the bonding of rhodium to delocalized hydrocarbon anions does not facilitate coupling. This may be seen from comparisons of $^1J(^{103}\text{Rh}-^{13}\text{C})$ for compounds containing σ -carbonyl (ca. 80 Hz),⁵⁸ π -olefin (10-16 Hz),⁵⁶ and π -cyclopentadienyl (0-5 Hz)^{55, 56, 58} ligands. Second, the ^{103}Rh nucleus apparently does not couple well with the ^1H nucleus even under the best of conditions. $^2J(^{103}\text{Rh}-^1\text{H})$ is only a little larger in σ -allylrhodium and methylrhodium compounds than in π -allylrhodium com-

pounds;⁵⁹ and, in a recently synthesized triphenylphosphinehydrido-rhodium compound, $^1J(^{103}\text{Rh}-^1\text{H})$ for the hydride nucleus was actually substantially smaller than $^2J(^{31}\text{P}-^1\text{H})$ for that nucleus.⁶⁰ Since nuclear spin-spin coupling is a through-bond phenomenon, the smallness of $^1J(^{103}\text{Rh}-^1\text{H})$ cannot be due to the nature of the Rh-H bond, which must transmit the ^{31}P coupling effects as well.

No metal-hydrogen coupling would be observed in the cobalt analog because, although ^{59}Co (100% natural abundance) has a spin of 7/2, its nuclear quadrupole moment is too large (0.5) to permit observable coupling. (Cf. ^{79}Br and ^{81}Br , both with $I = 3/2$, which have quadrupole moments of ca. 0.3.)⁶¹

The mass spectrum is mostly what one would predict: large peaks ascribable to the molecular ion, that ion minus $\text{C}_2\phi_2$ and $\text{C}_4\phi_4$, and ions of those two hydrocarbon fragments. Somewhat surprising, however, is a large peak at m/e 267, ascribable to the triphenylcyclopropenium ion. This peak is entirely absent in the mass spectrum of the cobalt analog.⁶²

EXPERIMENTAL

General Remarks

Reagent grade diphenylacetylene was obtained from Aldrich Chemical Company and was used without further purification. π -Cyclopentadienyl- π -1,5-cyclooctadienerhodium(I)⁶³ and its precursor, π -1,5-cyclooctadienerhodium(I) chloride dimer,⁶⁴ were prepared in 93% and 94% yields, respectively, according to published methods. The original source of rhodium, rhodium trichloride trihydrate, was obtained from Engelhard Industries.

Spectra were obtained on the following instruments: Beckman IR-10 infrared spectrophotometer, Cary 15 UV-visible spectrophotometer, Varian A60-A and XL-100 NMR spectrometers, Hitachi-Perkin-Elmer RME-6E single-focussing mass spectrometer. Elemental analyses were performed by PCR, Incorporated, Gainesville, Florida.

Preparation of π -Cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I)

In a typical experiment, a glass tube was charged with 3.00 g (16.8 mmol) of diphenylacetylene and 1.25 g (4.50 mmol) of π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) and sealed inside a 30-ml stainless steel Hoke bomb under nitrogen. The bomb was then heated to 180° for 48 hours. The resulting deep red reaction mixture was cooled and extracted with hexane. A white, insoluble solid was identified as hexaphenylbenzene (1.67 g, 55%) by its mass spectrum ($M^+ = 534$) and by its melting point (>400°, lit.⁶⁵ 454-5°). The red

hexane solution was chromatographed on alumina. Elution with hexane gave unreacted π -cyclopentadienyl- π -1,5-cyclooctadienerhodium(I) (1.04 g, 83%) and unreacted diphenylacetylene (0.97 g, 32%). Elution with hexane/benzene (5:1) gave π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) (64 mg, 0.3%). In other instances the yield of cyclobutadiene complex was as high as 3.3%. A small amount of orange-brown material remained of the column and could not be eluted.

The cyclobutadiene complex was a yellow, air-stable, crystalline compound which melted without apparent decomposition at $227-8^{\circ}$. (evacuated, sealed tube). It was stable in solution in hydrocarbons or CS_2 but was rapidly degraded to a deep red material by CCl_4 .

Analysis: Calculated for $\text{C}_{33}\text{H}_{25}\text{Rh}$: C, 75.57%; H, 4.80%. Found: C, 75.75%; H, 5.09%. The infrared spectrum (KBr pellet) displayed absorptions at 3060(w), 3030(w), 2930(w), 2870(vw), 1600(m), 1494(m), 1445(m), 1270(w), 1115(w), 1070(w), 1029(w), 871(w), 800(w), 766(m), 749(m), 700(s), 561(m) cm^{-1} . The UV spectrum in isooctane exhibited λ_{max} at 225 and 294 nm, with ϵ of 38700 and 31700, respectively. The mass spectrum consisted of the following major ions, listed as m/e(relative intensity): 524(100), 358(34), 356(48), 346(64), 279(25), 267(50), 178(42), 168(61), 167(28), 150(26), 105(20), 71(24), 69(26), 57(71), 56(38), 55(36). The ^1H NMR spectrum in CS_2 showed a multiplet at 2.9τ and a doublet at 4.99τ , relative areas 4:1. In C_6D_6 the lower field multiplet split into two multiplets at 2.4τ and 2.9τ , and the doublet shifted slightly upfield to 5.01τ (relative areas 8:12:5). The $^{103}\text{Rh}-^1\text{H}$ coupling constant was 1.1 Hz.

Attempted Thermal Trimerization of Diphenylacetylene

When pure diphenylacetylene was heated to 180° for 48 hours under nitrogen, it was recovered unchanged.

Crystal Data and Intensity Measurement

Preliminary Weissenberg and precession photographs indicated that the crystals were monoclinic; systematic absences of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ identified the space group as $P2_1/c$ (C_{2h}^5). Other crystal data were as follows: $M = 524.26$ ($C_{33}H_{25}Rh$), $a = 13.416(3)$, $b = 19.534(6)$, $c = 13.411(2)$ Å, $\beta = 135.01(1)^{\circ}$, $U = 2484.6(1.1)$ Å³, D_m (by flotation in a mixture of CCl_4 and cyclohexane) = 1.40 g/cm³, $Z = 4$, $D_c = 1.411$ g/cm³.

A suitable crystal was aligned on a Syntex $P\bar{I}$ automated diffractometer. Unit-cell dimensions were determined by a least-squares estimation of 15 reflections using molybdenum $K\alpha$ radiation ($\lambda = 0.71069$ Å) with a graphite monochromator. A variable-rate, θ - 2θ scan technique was used to measure all the independent reflections up to a 2θ limit of 50° . The scan rate varied from 1° /minute to 24° /minute, depending upon peak intensity. The background was measured at a point one degree to each side of the α_1 and α_2 peaks for a time equal to one quarter of the total scan time. The intensity, I , is equal to $\{[\text{total scan counts} - (\text{background count} / \text{background-to-scan ratio})] \times \text{scan rate}\}$ with a standard deviation, $\sigma(I)$, equal to $[\text{total scan counts} + (\text{background count} / \text{background-to-scan ratio})^2]^{\frac{1}{2}}$. The 3675 reflections which had $I \geq 1.2\sigma(I)$ were considered observed and were used in this analysis. The data were reduced to a set of structure factors on an arbitrary scale by the application of Lorentz polarization assuming that the monochromator was a 50% mosaic and 50% perfect crystal.

STRUCTURE DETERMINATION AND REFINEMENT

A sharpened, three-dimensional Patterson function was calculated from the observed structure amplitudes, and the position of the rhodium atom was deduced from this function. A first Fourier synthesis, using phase angles based only upon the rhodium atom, revealed all the carbon atoms in the cyclobutadiene ligand. A second Fourier synthesis, using phase angles derived from the 29 located atoms revealed the five carbon atoms of the cyclopentadienyl ligand. Three cycles of full-matrix least-squares fitting using isotropic thermal parameters reduced R , $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, to 0.074. An additional six cycles of least-squares refinement using a block-diagonal approximation and anisotropic thermal parameters further reduced R to 0.043. The largest shift in a positional parameter was approximately one third of the corresponding estimated standard deviation. Among the thermal parameters the greatest shift was that for β_{12} of C(A3), approximately two thirds of an estimated standard deviation. The majority of the shifts, however, were much smaller, and the refinement was terminated. A difference Fourier synthesis located the five cyclopentadienyl hydrogen atoms. No attempt was made to locate the phenyl hydrogen atoms. Table V lists the final positional and thermal parameters for the nonhydrogen atoms. The final cyclopentadienyl hydrogen parameters and their corresponding C-H distances are given in Table VI.

The quantity minimized in the least-squares calculations was

$\sqrt{w}(|F_O| - |F_C|)^2$, where $\sqrt{w} = |F_O|/4F_M$ if $|F_O| < 4F_M$, $w = 1$ if $4F_M \leq |F_O| \leq 6F_M$, $\sqrt{w} = 6F_M/|F_O|$ if $|F_O| > 6F_M$. In this case F_M , the mean minimum observable F_O , was 20.0. Scattering factors were taken from Hanson et al.⁶⁶ The rhodium atom was corrected for the real part of the anomalous dispersion factor. All calculations were performed on an IBM 360/65 computer with programs written or modified by Dr. Gus J. Palenik.

The table of structure factors has been deposited as NAPS Document No. 01983 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022.

DISCUSSION

Figure 1 gives a view of the π -cyclopentadienyl- π -tetraphenylcyclobutadienerhodium(I) molecule together with the atomic numbering. The cyclopentadienyl ring is planar within experimental error (see Table VII) with a rhodium-to-cyclopentadienyl-ring-plane distance of 1.868 Å. This compares favorably with the corresponding distance of 1.86 to 1.91 Å reported for other such complexes.⁶⁷⁻⁷⁵ The rhodium-to-carbon distances involving the five-membered ring vary from 2.202(10) to 2.229(7) Å (see Table VIII) with a mean value of 2.214(4) Å. This mean value also compares favorably with the 2.19 to 2.26 Å reported for other π -cyclopentadienylrhodium complexes.⁶⁸⁻⁷⁵ It is interesting to note that the two longest of these distances involve the two carbon atoms, C(8) and C(9), which nearly eclipse the C(3) and C(4) atoms of the other ligand, while the shortest involves the carbon atom C(6), the one nearly staggered with the other ligand. While these differences in rhodium-to-carbon distances may be too small to be significant, the pattern is the same as that observed in similar complexes.^{68,75} The difference in rhodium-carbon bond lengths indicates that the rings are not exactly parallel; the angle between them was calculated to be 2.4°. In the present compound and in three similar complexes just mentioned, the differences in rhodium-carbon distances are mirrored in the carbon-carbon bond lengths, i.e., the carbon atoms more loosely bonded to rhodium are more tightly bonded to each other. In the

cyclobutadiene complex this difference is not very pronounced; it is much more pronounced in the other complexes, particularly in π -cyclopentadienyl- π -ethylene- π -tetrafluoroethylenerrhodium(I).⁷⁵ The internal angles of the five-membered ring (see Table IX) vary from $107.0(7)^\circ$ to $109.7(8)^\circ$. Since the ring is planar, the mean value is 108° .

Two of the cyclopentadienyl hydrogen atoms appear to be displaced slightly toward the metal atom from the ring plane; the other three appear slightly displaced away from it. Since the hydrogen-atom positions were not refined, it is doubtful whether any significance may be attached to these displacements.

The mean carbon-carbon distance in the cyclobutadiene ligand is $1.470(4) \text{ \AA}$, not significantly different from the mean distances in tetraphenylcyclobutadiene complexes of iron ($1.459(7) \text{ \AA}$)⁷⁶ and molybdenum ($1.461(13) \text{ \AA}$,⁷⁷ $1.469(5) \text{ \AA}$)⁷⁶. The phenyl groups are bent away from the metal atom at a mean angle of 7.1° and are twisted about their bonds to the four-membered ring at angles of 42.8° , 42.8° , 32.2° , and 39.3° (rings A, B, C, and D, respectively). The relatively small twist angle of the C ring is probably an intermolecular effect, since no intramolecular phenomenon seems to account for it.

Within experimental error, the cyclobutadiene ring is planar, and the rhodium atom is equidistant from all four carbon atoms. The average distance is 2.103 \AA . The perpendicular distance from the metal atom to the ring plane is 1.828 \AA . The main point of interest with regard to the cyclobutadiene ligand is the establishment of its identity as a true cyclobutadiene and not an isomer.

FIGURE 1

A view of the molecule drawn by the ORTEP computer program. The enclosed areas are the 50% probability thermal ellipsoids.

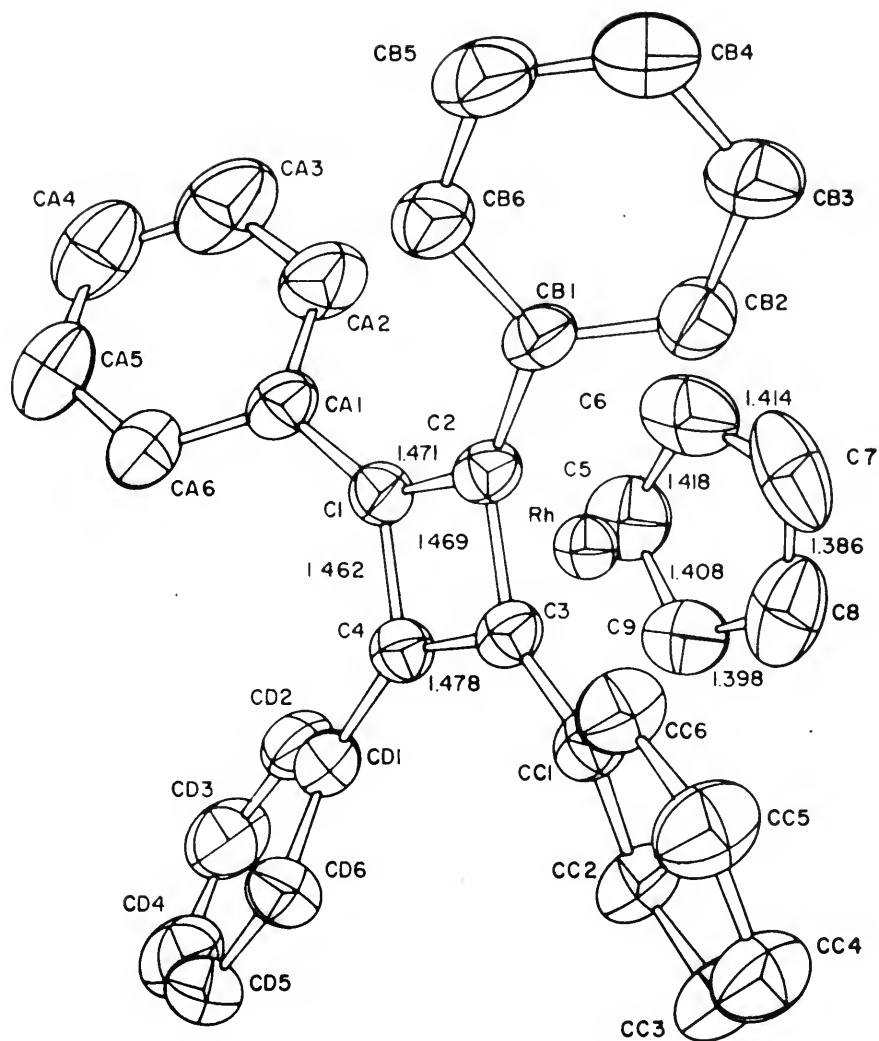


TABLE V
 ATOMIC PARAMETERS ($\times 10^4$) OF THE NONHYDROGEN ATOMS IN
 π -CYCLOPENTADIENYL- π -TETRAPHENYLCYCLOBUTADIENERHODIUM(I) (a)

Atom	\bar{x}	\bar{y}	\bar{z}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	2276(1)	1719(1)	2965(1)	83(1)	21(1)	77(1)	1(1)	118(1)	3(1)
C1	1780(4)	2560(2)	1697(4)	84(4)	21(1)	90(5)	8(4)	131(8)	10(4)
C2	1288(4)	1917(2)	896(4)	83(4)	22(1)	77(4)	10(3)	114(8)	10(3)
C3	2757(4)	1705(2)	1772(4)	94(4)	21(1)	81(4)	12(4)	133(8)	14(4)
C4	3245(4)	2350(2)	2579(4)	87(4)	20(1)	81(4)	5(4)	125(8)	10(4)
C5	2346(6)	1864(3)	4654(6)	181(8)	45(2)	130(7)	0(6)	262(13)	3(6)
C6	1081(6)	1521(4)	3496(6)	146(7)	68(3)	148(7)	- 6(7)	241(14)	29(7)
C7	1437(8)	884(4)	3315(7)	274(12)	48(2)	178(9)	-92(9)	362(19)	-16(7)
C8	2895(8)	836(3)	4360(7)	299(13)	36(2)	197(9)	42(8)	412(20)	61(7)
C9	3470(6)	1432(3)	5175(5)	146(7)	50(2)	100(6)	12(6)	183(12)	37(6)
CA1	1114(4)	3202(2)	1527(4)	101(5)	23(1)	96(5)	18(4)	144(9)	10(4)
CA2	- 94(6)	3203(3)	1270(7)	148(7)	39(2)	198(9)	51(6)	274(14)	44(7)
CA3	- 706(8)	3845(4)	1097(8)	217(10)	52(3)	232(11)	101(8)	373(19)	65(8)
CA4	- 128(8)	4445(3)	1182(7)	258(11)	37(2)	199(10)	94(8)	357(19)	50(7)

TABLE V - Continued

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
CA5	1070(7)	4442(3)	1442(6)	207(9)	29(2)	150(8)	50(6)	249(15)	29(6)
CA6	1687(5)	3819(2)	1609(5)	121(6)	24(1)	106(6)	16(5)	143(10)	10(4)
CB1	- 103(4)	1647(2)	- 387(4)	84(4)	24(1)	83(4)	16(4)	118(8)	15(4)
CB2	- 432(5)	955(3)	- 494(5)	110(6)	24(1)	107(6)	- 1(5)	104(10)	- 6(4)
CB3	-1757(5)	699(3)	-1707(6)	104(6)	35(2)	119(6)	- 8(5)	108(11)	-10(5)
CB4	-2734(5)	1136(3)	-2822(5)	97(6)	41(2)	103(6)	2(5)	122(10)	- 7(5)
CB5	-2422(5)	1818(3)	-2722(5)	106(6)	42(2)	99(6)	23(5)	144(10)	28(5)
CB6	-1119(5)	2079(3)	-1523(5)	106(6)	34(2)	96(5)	18(5)	132(10)	34(5)
CC1	3453(4)	1153(2)	1709(4)	97(5)	22(1)	89(5)	15(4)	140(9)	15(4)
CC2	4786(5)	928(3)	2915(5)	116(6)	29(1)	108(6)	39(5)	149(10)	28(5)
CC3	5440(6)	402(3)	2833(6)	134(7)	30(2)	144(7)	43(5)	194(12)	27(5)
CC4	4762(6)	100(3)	1554(6)	153(7)	31(2)	174(8)	33(6)	235(14)	8(6)
CC5	3441(6)	338(3)	332(6)	156(7)	33(2)	148(7)	22(6)	212(13)	-15(6)
CC6	2782(5)	861(3)	408(5)	119(6)	28(1)	105(6)	9(5)	152(10)	- 8(5)
CD1	4579(4)	2728(2)	3632(4)	83(5)	21(1)	98(5)	9(4)	118(8)	15(4)
CD2	4800(5)	3141(2)	4622(5)	96(5)	23(1)	111(6)	2(4)	115(9)	- 9(4)

TABLE V - Continued

Atom	x	y	z	$\frac{\beta_{11}}{11}$	$\frac{\beta_{22}}{22}$	$\frac{\beta_{33}}{33}$	$\frac{\beta_{12}}{12}$	$\frac{\beta_{13}}{13}$	$\frac{\beta_{23}}{23}$
CD3	6008(6)	3531(3)	5580(6)	121(7)	27(2)	159(8)	3(5)	121(13)	-14(6)
CD4	7015(6)	3510(3)	5539(8)	112(7)	31(2)	214(10)	7(6)	140(14)	32(7)
CD5	6822(5)	3105(3)	4562(7)	103(6)	36(2)	187(9)	7(5)	178(13)	46(6)
CD6	5608(5)	2697(3)	3612(6)	106(6)	33(2)	158(7)	15(5)	192(11)	41(5)

(a) The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE VI

ATOMIC PARAMETERS OF THE CYCLOPENTADIENYL HYDROGEN ATOMS

<u>Atom</u>	<u>Bonded to</u>	<u>Distance(Å)</u>	<u>x(a)</u>	<u>y(a)</u>	<u>z(a)</u>
H5	C5	1.06	270	233	524
H6	C6	0.98	10	166	295
H7	C7	1.07	61	56	248
H8	C8	0.95	338	46	440
H9	C9	0.97	449	144	592

(a) The positional parameters are $\times 10^3$.

TABLE VII
LEAST-SQUARE PLANES (a)

<u>Atoms</u>	<u>Planes</u>	
	<u>1</u>	<u>2</u>
C1	2*	3662
C2	- 2*	3667
C3	2*	3731
C4	- 2*	3731
C5	-3679	- 2*
C6	-3649	- 3*
C7	-3678	6*
C8	-3744	- 7*
C9	-3728	6*
H5		- 16
H6		- 91
H7		13
H8		61
H9		13
CA1	196	
CB1	136	
CC1	191	
CD1	183	
Rh	-1828	1868

TABLE VII - Continued

	<u>Parameters for the planes ($\times 10^4$) (b)</u>	
	<u>1</u>	<u>2</u>
l	6300	6615
m	4404	4234
n	-6397	- 6190
p	16611	-20258

- (a) The deviation from the plane ($\text{\AA} \times 10^3$) are given for the specified atom. The atoms used to define the plane are noted by an asterisk following the deviation. The dihedral angle between planes 1 and 2 is 2.4° .
- (b) Equation of the plane in the form: $\text{Deviation}(\text{\AA}) = lX + mY + nZ - p$, where X, Y, Z are the orthogonal coordinates (in \AA) relative to a, b, c^* , and p is the distance of the plane from the origin.

TABLE VIII
BOND LENGTHS (Å)

Rh - C1 = 2.104(4)	CA2 - CA3 = 1.425(11)
Rh - C2 = 2.098(4)	CA3 - CA4 = 1.366(12)
Rh - C3 = 2.106(6)	CA4 - CA5 = 1.382(16)
Rh - C4 = 2.104(6)	CA5 - CA6 = 1.399(9)
Rh - C5 = 2.218(8)	CA6 - CA1 = 1.391(8)
Rh - C6 = 2.202(10)	CB1 - CB2 = 1.398(7)
Rh - C7 = 2.214(10)	CB2 - CB3 = 1.402(8)
Rh - C8 = 2.229(7)	CB3 - CB4 = 1.382(8)
Rh - C9 = 2.225(5)	CB4 - CB5 = 1.374(9)
C1 - C2 = 1.471(6)	CB5 - CB6 = 1.388(8)
C2 - C3 = 1.469(8)	CB6 - CB1 = 1.397(6)
C3 - C4 = 1.479(6)	CC1 - CC2 = 1.384(8)
C4 - C1 = 1.463(8)	CC2 - CC3 = 1.406(10)
C5 - C6 = 1.419(10)	CC3 - CC4 = 1.381(8)
C6 - C7 = 1.414(12)	CC4 - CC5 = 1.391(10)
C7 - C8 = 1.386(14)	CC5 - CC6 = 1.401(10)
C8 - C9 = 1.398(9)	CC6 - CC1 = 1.400(6)
C9 - C5 = 1.408(11)	CD1 - CD2 = 1.393(7)
C1 - CA1 = 1.461(7)	CD2 - CD3 = 1.383(9)
C2 - CB1 = 1.476(6)	CD3 - CD4 = 1.391(15)
C3 - CC1 = 1.467(8)	CD4 - CD5 = 1.390(11)
C4 - CD1 = 1.473(7)	CD5 - CD6 = 1.405(10)
CA1- CA2 = 1.398(12)	CD6 - CD1 = 1.402(11)

TABLE IX

BOND ANGLES ($^{\circ}$)

C1 -C2 -C3 = 90.1(4)	C2 -C3 -CC1 = 135.1(5)
C2 -C3 -C4 = 89.7(4)	C4 -C3 -CC1 = 134.3(5)
C3 -C4 -C1 = 90.0(4)	C3 -CC1-CC2 = 121.0(5)
C4 -C1 -C2 = 90.2(4)	C3 -CC1-CC6 = 119.8(5)
C2 -C1 -CA1 = 135.2(5)	CC2-CC1-CC6 = 119.2(5)
C4 -C1 -CA1 = 133.6(5)	CC1-CC2-CC3 = 120.2(6)
C1 -CA1-CA6 = 119.2(5)	CC2-CC3-CC4 = 120.7(7)
C1 -CA1-CA2 = 120.9(6)	CC3-CC4-CC5 = 119.5(7)
CA2-CA1-CA6 = 119.8(6)	CC4-CC5-CC6 = 120.1(7)
CA1-CA2-CA3 = 118.5(7)	CC5-CC6-CC1 = 120.4(6)
CA2-CA3-CA4 = 120.8(8)	C3 -C4 -CD1 = 137.5(5)
CA3-CA4-CA5 = 120.5(8)	C1 -C4 -CD1 = 131.5(5)
CA4-CA5-CA6 = 119.8(7)	C4 -CD1-CD2 = 119.9(5)
CA5-CA6-CA1 = 120.6(6)	C4 -CD1-CD6 = 120.4(5)
C1 -C2 -CB1 = 134.4(5)	CD2-CD1-CD6 = 119.6(5)
C3 -C2 -CB1 = 135.0(5)	CD1-CD2-CD3 = 121.6(6)
C2 -CB1-CB2 = 120.8(5)	CD2-CD3-CD4 = 118.7(7)
C2 -CB1-CB6 = 120.7(5)	CD3-CD4-CD5 = 121.0(7)
CB2-CB1-CB6 = 118.6(5)	CD4-CD5-CD6 = 120.1(7)
CB1-CB2-CB3 = 120.9(6)	CD5-CD6-CD1 = 119.0(6)
CB2-CB3-CB4 = 119.2(6)	C5 -C6 -C7 = 108.4(7)
CB3-CB4-CB5 = 120.2(6)	C6 -C7 -C8 = 107.0(8)
CB4-CB5-CB6 = 121.1(6)	C7 -C8 -C9 = 109.7(8)
CB5-CB6-CB1 = 119.9(6)	C8 -C9 -C5 = 107.8(7)
	C9 -C5 -C6 = 107.0(7)

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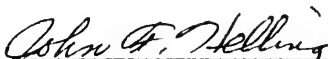
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BIOGRAPHICAL SKETCH

Gordon G. Cash was born June 14, 1947, in Lexington, Kentucky. In 1950 he and his parents moved to St. Petersburg, Florida. In June, 1965, he was graduated from St. Petersburg High School. In September, 1965, he enrolled in the University of Florida, where he obtained a Bachelor of Science degree with a major in chemistry in June, 1969. Immediately afterward, he enrolled in the Graduate School of that institution. He obtained a teaching assistantship from the Department of Chemistry while studying toward the degree of Doctor of Philosophy.

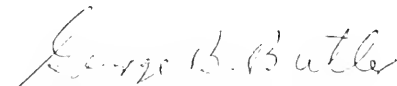
Gordon G. Cash was married to the former Jane Ann Clements on July 13, 1968.

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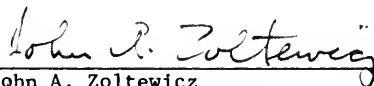
John F. Helling, Chairman
Associate Professor of
Physical Sciences and Chemistry

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George B. Butler
Professor of Chemistry

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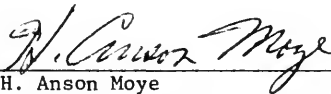
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1975

Dean, Graduate School

